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

Mechanism of the Polymerization of Acrylonitrile Initiated by the Mannitol/Cerium(IV) Redox System

N. Mohanty[a]; B. Pradhan[a]; M. C. Mahanta[a]
[a] Mayurbhanj Chemical Laboratory, Ravenshaw College, Cuttack, India

To cite this Article Mohanty, N. , Pradhan, B. and Mahanta, M. C.(1981) 'Mechanism of the Polymerization of Acrylonitrile Initiated by the Mannitol/Cerium(IV) Redox System', Journal of Macromolecular Science, Part A, 16: 8, 1413 — 1428

To link to this Article: DOI: 10.1080/00222338108063245

URL: http://dx.doi.org/10.1080/00222338108063245

J. MACROMOL. SCI.–CHEM., A16(8), pp. 1413-1428 (1981)

Mechanism of the Polymerization of Acrylonitrile Initiated by the Mannitol/Cerium(IV) Redox System

N. MOHANTY, B. PRADHAN, and M. C. MAHANTA

Mayurbhanj Chemical Laboratory
Ravenshaw College
Cuttack 753003, India

ABSTRACT

The mechanism of polymerization of acrylonitrile initiated by the mannitol-Ce(IV) redox system has been studied in aqueous sulfuric acid medium in the temperature range 30 to 40°C. Experimental findings show that when the ceric ion concentration is held low (0.00005-0.02 M), the mechanism of polymerization is consistent with the kinetic scheme involving initiation by primary radicals and termination by growing polymer radicals. But when the ceric ion concentration exceeds 0.02 M, the linear mode of termination seems to operate. The effect of certain salts, acids, solvents, and temperature on the rate of polymerization (R_p) and the rate of metal ion disappearance ($-R_{Ce}$) has also been investigated, and various rate and energy parameters have been evaluated.

INTRODUCTION

Different mechanistic pathways have been suggested by different workers [1, 2] to explain the experimental observation concerning redox polymerization of acrylonitrile (AN). In such mechanisms the mode of termination process has been the main subject of controversy [3]. Again, since ceric ions alone induces homopolymerization even in the absence of sensitizers [4-6], and also because it produces complexes with certain alcohols [7], the role played by it in the kinetic scheme is crucial to the overall mechanism.

To suppress the role of ceric ions alone in redox polymerization, some workers have used low temperature [8] and others have used very low concentrations of metal ions [9]. But using very low metal ion concentrations results in a low percentage of conversion and using low temperature is not always commercially advantageous. Experiments in this laboratory have shown that the mannitol-Ce(IV) redox pair is an efficient system for graft copolymerization of AN onto various natural polymers like Tusah silk. We have, therefore, investigated the mechanism of polymerization of AN in the presence of the mannitol/ceric(IV) redox pair while gradually varying the concentration of the ceric ion from very low (0.0005 $\underline{M}$) to moderately high (0.04 $\underline{M}$) values and at various temperatures (30 to 45°C) to find the optimum combination of temperature and metal ion concentration for subsequent application of the system to grafting experiments. The results of grafting experiments on Tusah silk will be reported separately.

EXPERIMENTAL

Materials

Acrylonitrile (Thomas Baker and Co., London) was purified by the method of Bamford et al. [10]. Such reagents as ceric ammonium sulfate, sulfuric acid, and mannitol were either BDH AnalaR or Merck G.R. varieties. Water, distilled twice over alkaline permanganate in an all-glass Corning unit, was used for the preparation of reagents and solutions. Reaction mixtures were deaerated by passing N_2 freed from O_2 by passage through several columns of Fieser's solution and then through a lead acetate solution. A tower containing conductivity water and AN of the same concentration was interposed between the reaction vessel and the system to compensate for any loss of monomer which might occur during flushing with N_2.

Polymerization Procedure

The polymerization reactions were carried out in Corning glass test tubes (100 mL) fitted with a $B_{24/29}$ ground joint head carrying inlet and outlet tubes for nitrogen. Appropriate quantities of the reaction mixture containing monomer, sulfuric acid, and mannitol were taken in the reaction vessel which was kept in a thermostat. The mixture was deaerated for 20 min and then the ceric solution, similarly

TABLE 1. Polymerization of Acrylonitrile by Various Ce(IV)/Alcohol Redox Systems[a]

Alcohol	Concentration (mol/L)	Induction period (min)	$10\ R_p$ (mol/L·s)
Nil	-	30	5.30
Glycerol	0.2125	1.56	13.74
Mannitol	0.2125	0.5	14.10
Sorbitol	0.2125	0.1	20.03

[a] Other conditions: [Ce(IV)] = 0.03 M; [AN] = 0.751 M; [H_2SO_4] = 0.8 M; ionic strength, μ = 3.04 M, temperature = 40° C.

deaerated, was added. The polymerization started after an induction period. After a specified time interval the reaction was arrested by the addition of known excess of ferrous ammonium sulfate solution. The polymer was filtered off, washed with water, and dried to constant weight. The rate of polymerization was calculated from the slope of the plot of yield versus time. The disappearance of ceric was followed titrimetrically.

RESULTS AND DISCUSSION

Induction Period

An induction period of 0.5 min was noted at 40° C before polymerization started. The point of the first appearance of turbidity in the reaction mixture from the start of the reaction was taken as the induction period. The first appearance of turbidity was determined refractometrically [11]. The induction period and the rate of polymerization (R_p) for different ceric-alcohol redox systems at 40° C are listed in Table 1. It is observed that under identical condition the order of reactivity of alcohols is sorbitol > mannitol > glycerol. A similar observation has been recorded by Rout et al. at another temperature [3] and with another redox system [12].

Relation between Conversion and Reaction Time

The relation between the percentage of conversion and reaction time for polymerization of AN initiated by the mannitol-ceric ion

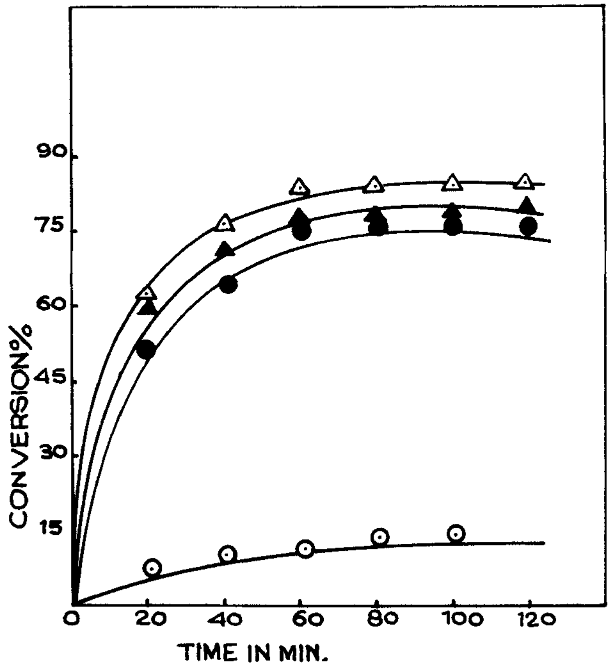

FIG. 1. Relation between % conversion and time (steady-state). [Ce(IV)] = 0.005 M, [M] = 0.751 M, T = 35°C, [H_2SO_4] = 0.5 M, μ = 1.69 M, (⊙) [R] = 0.0 M, (●) [R] = 0.0125 M, (▲) [R] = 0.025 M, (△) [R] = 0.05 M.

redox system is shown in Fig. 1. A limiting conversion is attained within 60 min. The percentage conversion has also been studied at different concentrations of the substrate (mannitol). The conversion increases with an increase of mannitol concentration as expected.

Rate of Polymerization

The relation between rate of polymerization (R_p) and [Ce(IV)] is shown in Fig. 2 (a and b). The rate increased progressively from [Ce(IV)] = 0.00005 M up to 0.0002 M and thereafter the rate rose abruptly and parabolically. At [Ce(IV)] > 0.005 M the rate was practically independent of [Ce(IV)], but at still higher concentrations (>0.02 M) the rate again fell. This behavior of ceric ion rules out the possibility of a linear mode of termination and points to the mutual mode of termination at least up to [Ce(IV)] = 0.02 M. Similar observations have been noted by us for the Ce(IV)-sorbitol redox system

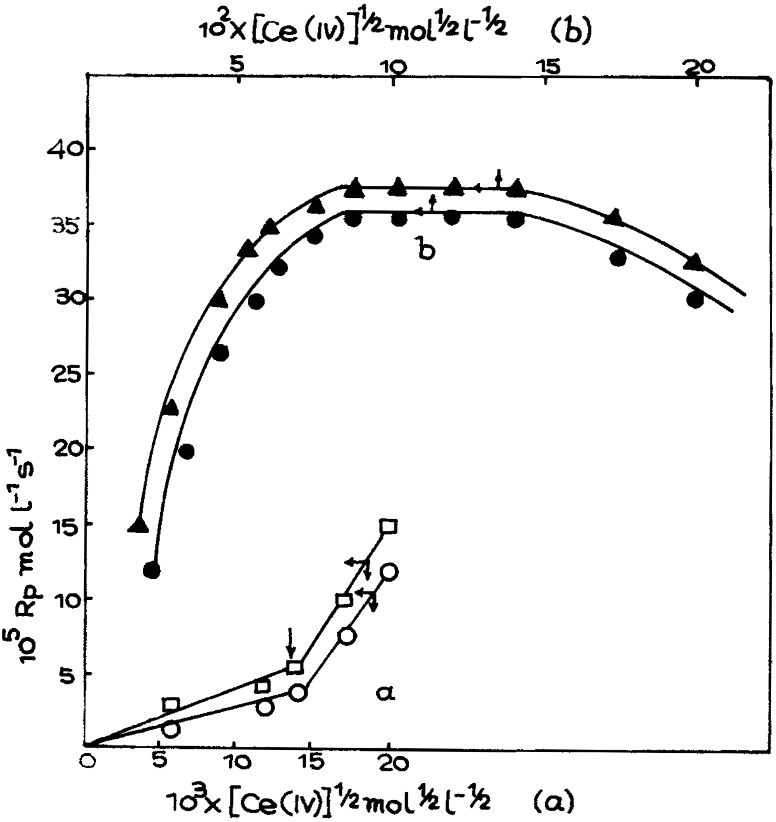

FIG. 2. (a) Variation of R_p with $[Ce(IV)]^{1/2}$ at low concentrations. [R] = 0.025 M, [M] = 1.502 M, [H_2SO_4] = 0.8 M, μ = 3.12 M, (○) at 35°C, (□) 40°C. (b) Variation of R_p with $[Ce(IV)]^{1/2}$ at high concentrations. [R] = 0.025 M, [M] = 1.502 M, [H_2SO_4] = 0.8 M, μ = 3.12 M, (●) = at 35°C, (▲) at 40°C.

[13]. Based on the above behavior of ceric ions, other experiments were planned.

At low concentrations, [Ce(IV)] = 0.00005 M, R_p increased progressively with increasing monomer concentration. Plots of R_p versus [M] were linear, passing through the origin (Fig. 3), and hence the order with respect to M was 1. R_p also varied linearly with the square root of the concentration of the substrate (R) (Fig. 4).

At high concentrations, [Ce(IV)] (0.005 M), R_p increased with

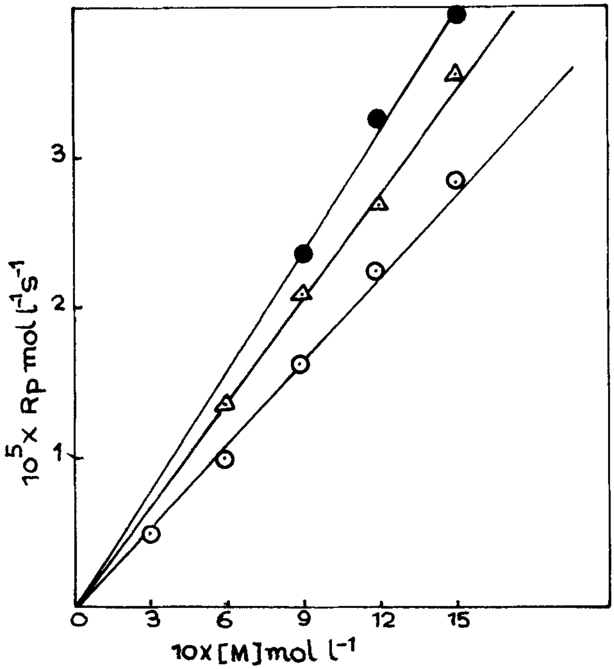

FIG. 3. Variation of R_p with [M], [Ce(IV)] = 0.00005 M, [R] = 0.025 M, [H_2SO_4] = 0.3 M, μ = 1.009 M, (⊙) at 30°, (▲) at 35°, (●) at 40°C.

increasing monomer concentration as before. Plots of R_p versus $[M]^{3/2}$ were linear, passing through the origin, and hence the order with respect to M was 1.50 (Fig. 5). R_p was found to decrease with an increase of [H_2SO_4] when the ionic strength μ was not kept constant. It also decreased with an increase of ionic strength, adjusted with $NaHSO_4$ or Na_2SO_4 at constant [H_2SO_4].

Rate of Ceric Ion Disappearance

Plots of [M] versus disappearance of ceric ions ($-R_{Ce}$) are shown in Fig. 6. The rate was found to be almost independent of [M], implying a negligible contribution of ceric ions in initiation reactions of the type M + Ce(IV). Similar observations have been made by us for the cerium-sorbitol redox system [13].

Plots of ceric ion disappearance versus ceric ion concentration

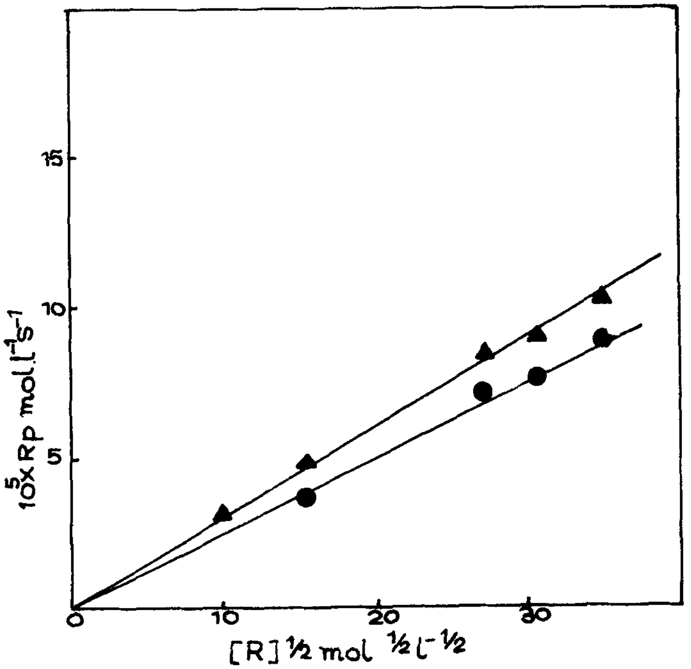

FIG. 4. Variation of R_p with $[R]^{1/2}$. [Ce(IV)] = 0.0001 M, $[H_2SO_4]$ = 4 M, [M] = 1.502 M, μ = 1.30 M, (●) at 35°, (▲) at 40°C.

are shown in Fig. 7. A first-order dependence of the rate on [Ce(IV)] is concluded from the linear plots of $(-R_{Ce})$ versus [Ce(IV)] passing through the origin. Plots of rate of ceric ion disappearance versus substrate (mannitol) concentration are shown in Fig. 8. An increase in the concentration of mannitol increased the rate. Plots of log $(-R_{Ce})$ versus log R gave a straight line with a small intercept.

The rate of disappearance of ceric ions was found to decrease with an increase of $[H_2SO_4]$ when the ionic strength was not maintained. It was also depressed when the ionic strength was adjusted with $NaHSO_4$, Na_2SO_4, etc. at constant $[H_2SO_4]$.

Rate Dependence on Temperature

The R_p and the rate of disappearance of ceric ions increased with an increase of temperature from 30 to 40°C. Similar effects have been noted by us [13] and Rout [14]. Such effects have been explained by Whitby et al. [15] in accordance with the Arrhenius theory.

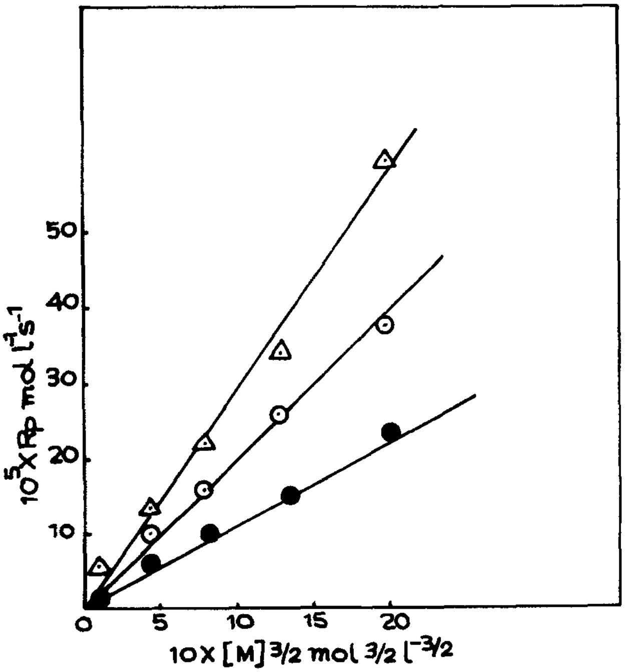

FIG. 5. Variation of R_p with $[M]^{3/2}$. [Ce(IV)] = 0.005 M, [R] = 0.025 M, [H_2SO_4] = 0.3 M, μ = 1.09 M, (●) at 30°, (⊙) at 35°, (▲) at 40° C.

Effect of Organic Solvents

The addition of small amounts (5% v/v) of organic solvent, e.g., methanol, acetone, and dioxane, depressed the initial rate of polymerization. This result has been explained by Schulz et al. [16] by supposing an increasing radical formation which simultaneously renders the termination rate relatively faster than the rate of growth of polymerization.

Reaction Mechanism and Rate Law

In the present investigation, we propose the following mechanism to explain our experimental results.

Primary radical formation:

$$\mathrm{Ce(IV)} + \mathrm{R} \xrightarrow{k_r} \mathrm{Ce(III)} + \mathrm{R^{\bullet}} + \mathrm{H^+} \qquad (1)$$

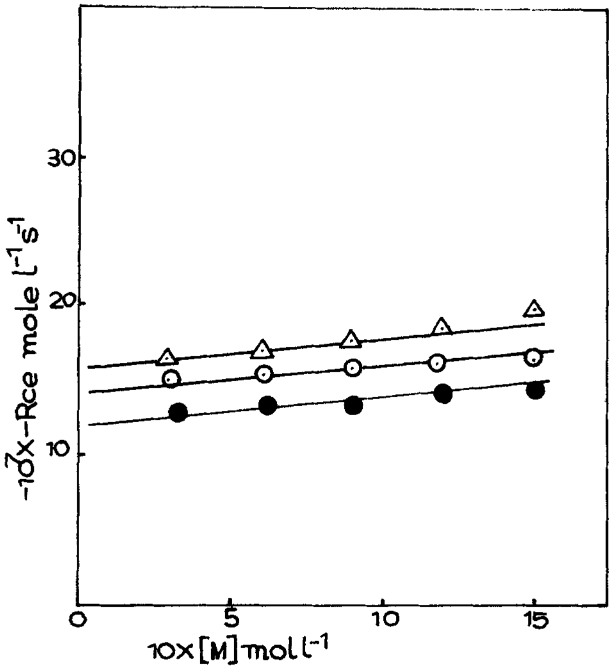

FIG. 6. Variation of $-(R_{Ce})$ with [M]. [Ce(IV)] = 0.005 M, [R] = 0.025 M, $[H_2SO_4]$ = 0.3 M, μ = 1.09 M, (●) at 30°, (⊙) at 35°, (△) at 40°C.

where R is an organic substrate and R• is a primary radical.

Initiation:

(a) By primary radical:

$$R^{\bullet} + M \xrightarrow{k_i} R\text{–}M^{\bullet} \qquad (2)$$

where M is a monomer and R–M• is the radical formed by the reaction of a primary radical with a monomer.

(b) By ceric ion:

$$Ce(IV) + M \xrightarrow{k_i'} M^{\bullet} + Ce(III) + H^+ \qquad (3)$$

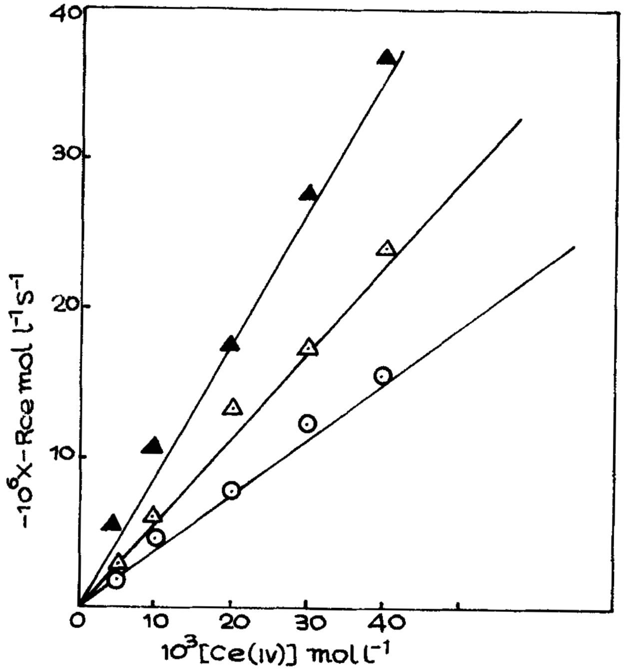

FIG. 7. Variation of $-R_{Ce}$ with [Ce(IV)]. [R] = 0.025 M, [M] = 1.502 M, [H_2SO_4] = 0.8 M, μ = 3.12 M, (⊙) at 30°C, (△) at 35°, (▲) at 40°C.

Propagation:

$$\text{R–M}^{\bullet} + \text{M} \xrightarrow{k_p} \text{R–M}_2^{\bullet}$$

$$\vdots$$

$$\text{R–M}_{n-1}^{\bullet} + \text{M} \xrightarrow{k_p} \text{R–M}_n^{\bullet} \tag{4}$$

where $M_n^{\bullet}$ is the growing polymer radical.

Termination:

(a) Linear by ceric ions:

$$\text{R–M}_n^{\bullet} + \text{Ce(IV)} \xrightarrow{k_{td}} \text{polymer} \tag{5}$$

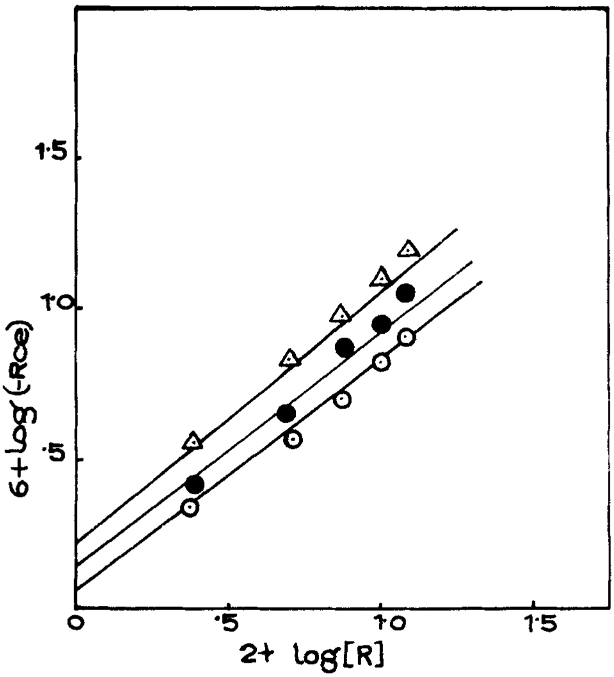

FIG. 8. Variation of $-R_{Ce}$ with [R] at [H_2SO_4] = 0.4 M, [M] = 0.751 M, [Ce(IV)] = 0.005 M, μ = 1.35 M, (⊙) at 30°, (●) at 35°, (▲) at 40°C.

(b) Mutual by combination:

$$R\text{–}M_n^{\bullet} + R\text{–}M_n^{\bullet} \xrightarrow{k_{tc}} \text{polymer} \tag{6}$$

(c) Primary radical termination:

$$M_n^{\bullet} + R^{\bullet} \xrightarrow{k_{t_p}} \text{polymer} \tag{7}$$

Primary radical reaction:

$$R^{\bullet} + \text{Ce(IV)} \xrightarrow{k_0} \text{products} + \text{Ce(III)} + H^{+} \tag{8}$$

After making the usual assumptions for steady-state concentrations for primary and chain radicals, the following expressions for

R_p and $-R_{Ce}$ can be derived for the three different types of terminations:

(a) *Mutual termination:*

$$R_p = \frac{K_p[M]^{3/2}[Ce(IV)]^{1/2}}{K_{t_c}^{1/2}} \left(\frac{K_r[R]}{[M] + (K_0/K_i)[Ce(IV)]} \right)^{1/2} \qquad (9)$$

$$-R_{Ce} = K_r[Ce(IV)][R] \qquad (10)$$

(b) *Linear termination:*

$$R_p = \frac{K_p[M]^2}{K_{t_d}} \left(\frac{K_r[R]}{[M] + (K_0/K_i)[Ce(IV)]} \right) \qquad (11)$$

$$-R_{Ce} = 2K_r[Ce(IV)][R] \qquad (12)$$

(c) *Primary radical termination:*

$$R_p = \frac{K_p K_i [M]^2}{K_{t_p}} \qquad (13)$$

$$-R_{Ce} = K_r[Ce(IV)][R] \qquad (14)$$

Although linear termination of vinyl polymerization is well recognized, the proportionalities experimentally realized in the present case point to mutual termination. Mutual termination has also been suggested by Santappa et al. [17]. Hence other modes of termination (linear and primary radical terminations) have been discarded in the present case.

At a very low concentration of Ce(IV) (0.00005 M), we can suppose that $(K_0/K_i)[Ce(IV)] \ll [M]$; then Eq. (9) reduces to

$$R_p = k_p \left(\frac{k_r}{k_{t_c}} \right)^{1/2} [R]^{1/2}[Ce(IV)]^{1/2}[M] \qquad (15)$$

Equation (15) explains the initial dependence of R_p on $[Ce(IV)]^{1/2}$ (Fig. 2a), the linear plots of R_p vs $[M]$ (Fig. 3), and the linear plots of R_p vs $[R]^{1/2}$ (Fig. 4) at low $[Ce(IV)]$.

At moderately high [Ce(IV)] concentrations (0.005-0.04 M), we can suppose $(K_0/K_i)[\mathrm{Ce(IV)}] \gg [M]$ and approximate the denominator of Eq. (9) to be $(K_0/K_i)[\mathrm{Ce(IV)}]$ and thereby obtain

$$R_p = K_p\left(\frac{K_rK_i}{K_0Kt_c}\right)^{1/2}[M]^{3/2}[R]^{1/2} \tag{16}$$

This expression is free of the term [Ce(IV)] and explains why the plot of R_p vs $[M]^{3/2}$ is linear and passes through the origin (Fig. 5).

At a very high [Ce(IV)] concentration (0.02 M), termination by Ce(IV) is possible. The downward plunge of the curve of R_p vs $[\mathrm{Ce(IV)}]^{1/2}$ (Fig. 2b) for $[\mathrm{Ce(IV)}] > 0.02$ M can be explained by supposing termination of polymerization by Ce(IV) alone. Similar observations have been made by us [13] and Rout et al. [3].

The decrease of R_p and $-R_{Ce}$ on increasing $[H_2SO_4]$ and $[SO_4^{-2}]$ can be explained by supposing the destruction of the neutral $Ce(SO_4)_2$ species by complexation. Similar arguments have been advanced by Santappa [17] for the active species of Ce(IV) in H_2SO_4.

Infrared Spectra

The IR spectra of the isolated and dehydrated polymer was determined following the method of Horback et al. [18] to detect end groups. The spectra showed aliphatic hydroxyl absorption at 3400 cm^{-1} along with peaks characteristic of the homopolymer of AN at 1015, 1245, 1445, and 2100 cm^{-1}. The heavy quenching of the $-C{\equiv}N$ absorption intensity at 2100 cm^{-1} is explained [19] as being due to the introduction of an oxygenated group into the molecule. The shifting of the narrow high intensity band at 3600 cm^{-1} to a wide high intensity band at 3400 cm^{-1} due to $-OH$ stretching is explained as being due to hydrogen bond formation. This observation confirms the proposed kinetic scheme that under the experimental conditions, initiation of polymerization is due to the primary radical formed from the substrate and termination is mutual due to a combination of growing polymer radicals.

Evaluation of Rate Parameters

Values of the rate parameters K_r were obtained from the slopes of plots of K_{obs} vs [R]. K_{obs} is a pseudo-first-order rate constant for ceric ion disappearance at a particular mannitol concentration.

Squaring both sides of Eq. (15), taking reciprocals, and rearranging, we get

TABLE 2. Rate Parameters of Acrylonitrile in the Presence of Mannitol and Ceric Ions

Temperature (°C)	$10^4 \times K_r$	$10^2 \times K_0/K_i$ from		$K_p/K_t^{1/2}$ from	
		$\frac{[M]^2}{R_p^2}$ vs $\frac{1}{[M]}$	$\frac{[M]^2}{R_p^2}$ vs $\frac{1}{[Ce(IV)]}$	$\frac{[M]^2}{R_p^2}$ vs $\frac{1}{[M]}$	$\frac{[M]^2}{R_p^2}$ vs $\frac{1}{[Ce(IV)]}$
30	0.3875	2.1428	2.0277	0.5388	0.5403
35	0.6125	2.4285	2.4263	0.5372	0.5387
40	0.9250	2.8750	2.8553	0.6356	0.6535

$$\frac{[M]^2}{R_p^{\,2}} = \frac{K_i}{K_p^{\,2}K_r[R][Ce(IV)]} + \frac{K_0K_t}{K_p^{\,2}K_rK_i[R][M]} \tag{17}$$

Values of the composite rate constants K_0/K_i were obtained from Eq. (17) by plotting either

$$\frac{[M]^2}{R_p^{\,2}} \text{ vs } \frac{1}{[M]} \quad \text{or} \quad \frac{[M]^2}{R_p^{\,2}} \text{ vs } \frac{1}{[Ce(IV)]}$$

and then substituting proper experimental values in the slope/intercept and intercept/slope expressions. Values of $K_p/K_t^{1\ 2}$ were obtained from the values of the slope and intercept of the former two plots by substitution of the proper experimental values.

The close conformity in the values of these rate parameters obtained in an alternative manner (Table 2) further supports the proposed kinetic scheme.

Energy Parameters

The values of E_r, $E_0 - E_i$, and $E_p - \frac{1}{2}E_t$ were computed to be 13.288, 5.1787, and 5.008 kcal/mol. The value of E_t was computed by taking standard values of E_p from the literature to be 1.976 kcal/mol. The corresponding entropies of activation for K_r, K_0/K_i, and $K_p/K_t^{1/2}$ were evaluated to be -32.17, -32.85, and -44.78 eu, respectively.

ACKNOWLEDGMENT

One of the authors (M.C.M.) is thankful to be UGC, New Delhi, India, for grant of a Teacher Fellowship.

REFERENCES

[1] G. Mino, S. Kaizermann, and E. Rasmussen, J. Polym. Sci., 38, 393 (1959).

[2] N. Mohanty, B. Pradhan and M. C. Mahanta, Eur. Polym. J., 15, 743 (1979).

[3] A. Rout, S. P. Rout, B. C. Singh, and M. Santappa, Makromol. Chem., 178, 639 (1977).

[4] H. F. Park, U.S. Patent 2,485,535 (October 18, 1949).

[5] G. N. Richards, J. Appl. Polym. Sci., 5, 539 (1961).

[6] J. Saldick, J. Polym. Sci., 19, 73 (1956).

[7] H. F. Offner, Doctoral Thesis, Stanford University, 1957.

[8] A. Rout, S. P. Rout, B. C. Singh, and M. Santappa, Eur. Polym. J., 13, 497 (1977).

[9] S. V. Subramanian and M. Santappa, J. Polym. Sci., A-1, 6, 493 (1968).

[10] C. H. Bamford and A. D. Jenkins, Proc. R. Soc. (London), A216, 515 (1953).

[11] M. A. Naylon and F. W. Billmeyer, J. Am. Chem. Soc., 75, 2181 (1953).

[12] A. Rout, B. C. Singh, and M. Santappa, Makromol. Chem., 177, 2709 (1976).

[13] N. Mohanty, B. Pradhan and M. C. Mahanta, Eur. Polym. J., 16, 451 (1980).

[14] A. Rout, S. P. Rout, N. Mallik and B. C. Singh, J. Polym. Sci., Polym. Chem. Ed., 16, 391 (1978).

[15] G. S. Whitby, M. D. Gross, J. R. Miller and A. J. Costanza, J. Polym. Sci., 16, 519 (1955).

[16] R. Schulz, G. Tenner, A. Hengleim, and W. Kern, Makromol. Chem., 12, 20 (1954).

[17] S. V. Subramanian and M. Santappa, J. Polym. Sci., A-1, 6493 (1968).

[18] A. Horback, U. Veiel, and H. Wunderlich, Makromol. Chem., 88, 215 (1965).

[19] L. J. Bellamy, Infrared Spectra of Complex Molecules, Methuen, London, 1956, p. 225.

Accepted by editor October 29, 1980
Received for publication December 8, 1980