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Polymerization of Acrylonitrile with Ceric Ion-2-Propanethiol as Initiator System

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ABSTRACT

The kinetics of the polymerization of acrylonitrile with ceric ammonium sulfate in the presence of 2-propanethiol as the redox initiator system in aqueous solution has been investigated. The rate of polymerization was found to be proportional to the square root of both ceric ion and thiol concentrations, and the monomer exponent was close to 1.5. Spectral studies indicated that there is a complex formation between ceric ion and the monomer acrylonitrile. A kinetic scheme, based on initial formation of this complex and its subsequent reaction with the thiol to produce the free radicals (RS•) responsible for initiation has been postulated to account for the observed results. The activation energy and different kinetic and transfer constants for the system have also been evaluated.

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INTRODUCTION

Thiols are known to be easily oxidized to disulfides. Wallace [1] studied the reaction between thiols and ferric soaps in organic solvents and found a rapid oxidation-reduction reaction involving intermediate thiyl (RS·) radicals. McAuley and co-workers [2, 3] also observed a similar formation of intermediate free radicals in the ceric ion oxidation of thiolic compounds in aqueous solution. Thiols in combination with suitable oxidizing agents can thus form effective redox initiator systems for polymerization of monomers. Most of the studies in this connection have used thiourea, a potential thiol by tautomerization, in combination with a number of familiar oxidizing agents such as peroxides, Fe^{3+}, bromate, persulfate, and Ce^{4+} etc. as initiators in aqueous solution [4-8]. Mandal et al. [9-11] used the $Fe(ClO_4)_3$-thiourea system for initiating polymerization in nonaqueous media.

Ordinary mercaptans have been studied only occasionally as redox initiators in vinyl polymerization. Recently a few studies appeared on the aqueous polymerization of acrylamide with ceric ion in the presence of some thiolic compounds, such as thiomalic acid [12], L-cysteine [13], and 2-mercaptoethanol [14] as redox initiator systems. The use of thiols in combination with dimethylsulfoxide [15, 16] and ferric laurate [17, 18] as redox initiators in nonaqueous media has also been demonstrated. We thus thought that a systematic investigation of the effect of different aliphatic mercaptans in combination with suitable metal ions as redox initiators would be highly interesting. In the present paper we report a detailed study of the aqeuous polymerization of acrylonitrile with ceric ammonium sulfate in the presence of 2-propanethiol as the redox initiator system.

EXPERIMENTAL

Materials

Acrylonitrile (BDH) was purified according to the method of Bamford et al. [19]. 2-Propanethiol (Aldrich Chemical Corp., U.S.A.) was obtained as pure reagent and was used as received. It was always stored under nitrogen. Dimethylformamide was dried over anhydrous sodium sulfate and fractionally distilled twice, the middle cut portion boiling at 150.5-151°C being collected each time for use in viscosity measurements. A stock solution of 0.05 M ceric ammonium sulfate in 1 M sulfuric acid was used for preparing the experimental recipes. The reactions were run under deaerated conditions. The deaeration was done by flushing the experimental systems with nitrogen which had been purified by passing through several columns of Fieser's solution, then through lead acetate solution, and finally dried by passing through a tower of concentrated sulfuric acid. Doubly distilled water, boiled for some time to remove any dissolved gas and further deaerated by passing purified nitrogen through it, was used for preparing polymerization recipes and all the standard solutions.

Polymerization Procedure

The polymerizations were carried out in 100 mL Pyrex conical flasks fitted with B-24 standard joint stoppers. Before the start of the experiment, the reaction vessel was flushed with nitrogen for 30 min, and measured amounts of monomer and thiol (deaerated separately) solutions in deaerated water were introduced into it, and the stopper replaced immediately. The reaction vessel was then placed in a water bath kept at the required temperature (to within ±0.05°C) and allowed to attain the temperature of the bath. The required amount of ceric ammonium sulfate stock solution was then introduced quickly, and the components were mixed by shaking and subsequently left undisturbed. There was a short induction period after which polymerization started, which was indicated by the appearance of turbidity in the initially clear solution. The turbidity increased with time of polymerization, and the polymer finally precipitated out. The polymerization was stopped at required intervals by taking the vessel out of the bath and introducing 50 mL of 1% hydroquinone solution. The contents were then poured into a large volume of water and the precipitated polymer was filtered through a weighed, sintered Gooch crucible, washed thoroughly with warm water, and dried at 40°C under vacuum to constant weight.

Purification of Polymer

The polymer was dissolved in a minimum quantity of pure dimethylformamide and reprecipitated by adding an excess of pure, dry methanol. It was then filtered through a G-4 Gooch crucible, washed repeatedly with methanol, and then dried under vacuum to constant weight. The polymer thus purified was used for molecular weight determination.

Molecular Weight Determination

The molecular weight (M) was determined viscometrically using the relation $[\eta] = KM^{\alpha}$, where $[\eta]$ is the intrinsic viscosity, and K and α are constants equal to 2.78×10^{-4} and 0.76, respectively, for polyacrylonitrile in N,N-dimethylformamide solution [20]. The viscometric measurements were done at 35°C (± 0.01°C) with an Ubbelohde suspended level dilution viscometer.

Spectrophotometric Study

Spectrophotometric measurements were carried out in a PYE-UNICAM-SP8-150 UV/VIS spectrophotometer.

RESULTS

The polymerization of acrylonitrile initiated by ceric ammonium sulfate in sulfuric acid in the presence of 2-propanethiol was carried

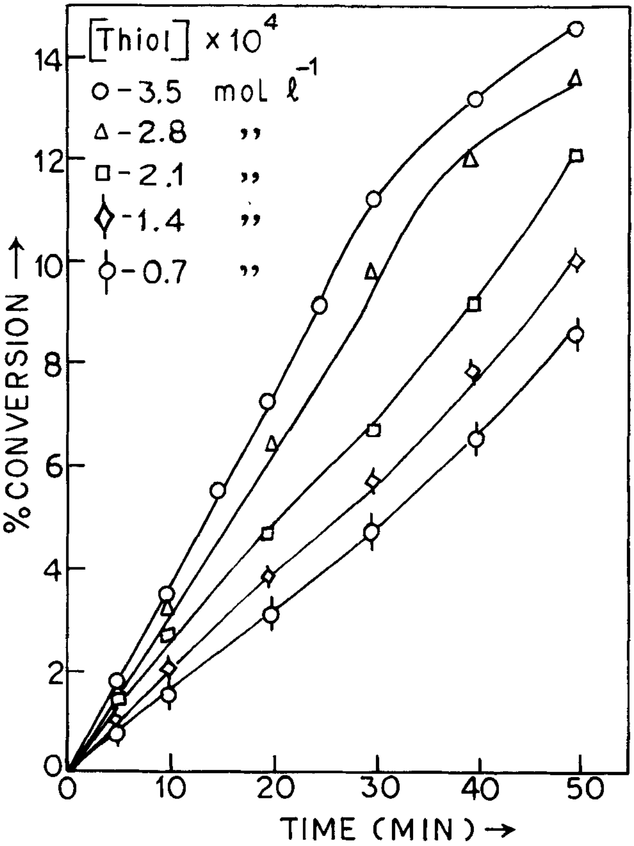

FIG. 1. Ceric ammonium sulfate-2-propanethiol initiated polymerization of acrylonitrile: Effect of 2-propanethiol concentration. Temperature = 30°C, $[H_2SO_4] = 1.66 \times 10^{-1}$ mol/L, $[Ce(IV)] = 8.33 \times 10^{-4}$ mol/L, [M] = 0.8506 mol/L.

out in aqueous solution at 30, 35, and 40°C. There is an induction period (usually not more than 5 min) which is more or less reproducible, and the onset of polymerization is indicated by the appearance of turbidity in the solution. The time of polymerization is, therefore, calculated from this point. There was no polymerization even after 1 h in the absence of the thiol under the conditions of the experiment. The polymerization experiments in the present study were, therefore, not run beyond 1 h so that any initiation by ceric ion alone could be ruled out. A typical set of reaction curves for 30°C showing the effect of varying 2-propanethiol concentration (0.7×10^{-4} to 3.5×10^{-4} mol/L) at constant ceric ion (8.33×10^{-4} mol/L) and monomer (0.8506 mol/L) concentrations on the polymerization yield at constant acid strength of the medium is shown in Fig. 1. It can be seen that the rate of polymerization increases with increasing thiol concentration. The induction period showed a decreasing trend with increasing thiol concentration. The rate of polymerization (R_p) was calculated from the initial slope of the corresponding yield-time curve. The order of the reaction with respect to 2-propanethiol concentration was determined from the slope of the double logarithmic plot of R_p vs 2-propanethiol concentration, which was found to be 0.5 (Fig. 2). The relationship between R_p and ceric ion concentration is shown in Fig. 3. Here also the normal half-order dependence of R_p on the ceric ion concentration is observed. The influence of monomer concentration on the rate was next studied to determine the overall polymerization rate equation. Figure 4 shows that the monomer exponent is approximately equal to 1.5. The effects of varying sulfate ion and H^+ ion concentrations were also studied, and the results are reported in Tables 1 and 2, respectively. The concentration of sulfate ion was varied by adding sodium sulfate.

The values of R_p at 30, 35, and 40°C have been utilized for the computation of the overall activation energy for the polymerization reaction. Figure 5 shows the Arrhenius plot of log R_p against 1/T, from the slope of which the overall activation energy was calculated to be 4.6 kcal/mol.

The effects of varying the thiol, ceric ion, and monomer concentrations on the degree of polymerization $\overline{DP}$ of polymer is shown in Table 3. It was found that $\overline{DP}$ increases with increasing monomer concentration but decreases with increasing thiol and ceric ion concentrations. $\overline{DP}$ measurements were usually made on polymer samples obtained at low conversions (less than about 5%).

Figure 6 shows the changes in the absorbance at 316 nm that occur on addition of varying concentrations of acrylonitrile (0.05-0.20 mol/L) to a Ce(IV) solution (2.5×10^{-4} mol/L) at a fixed H_2SO_4 concentration (0.16 mol/L). This indicates complex formation between Ce(IV) and

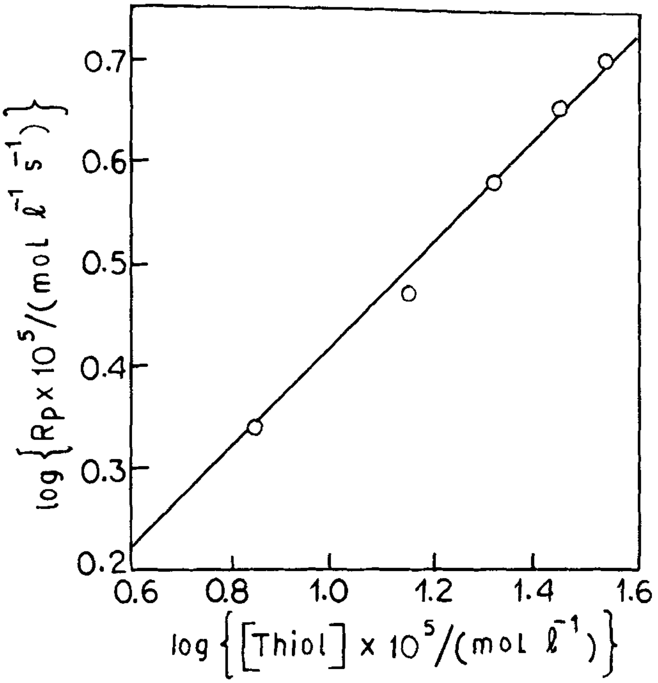

FIG. 2. Relationship between log R_p and log [2-propanethiol]. Temperature = 30°C, $[H_2SO_4] = 1.66 \times 10^{-1}$ mol/L, [Ce(IV)] = 8.33×10^{-4} mol/L, [M] = 0.8506 mol/L.

TABLE 1. Effect of Sulfate Ion on the Rate of Polymerization at 30°C[a]

$[Na_2SO_4] \times 10^2$, mol/L	Initial rate, $R_p \times 10^6$, mol/L·s
Nil	50.0
1.2	38.6
2.4	28.3
3.6	22.4
4.8	15.3

[a] [M] = 0.8506 mol/L, [Ce(IV)] = 8.33×10^{-4} mol/L, $[H_2SO_4]$ = 1.66×10^{-1} mol/L, [2-propanethiol] = 3.5×10^{-4} mol/L.

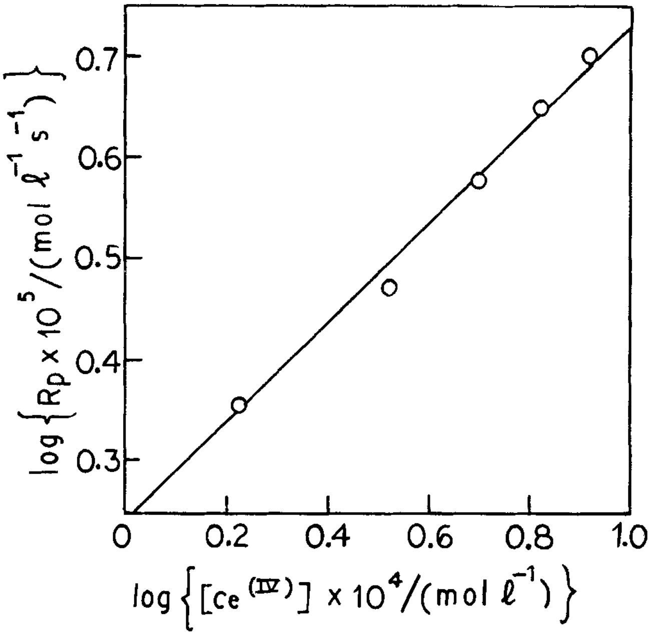

FIG. 3. Relationship between log R_p and log [Ce(IV)]. Temperature = 30°C, $[H_2SO_4] = 1.66 \times 10^{-1}$ mol/L, [2-propanethiol] = 3.5×10^{-4} mol/L, [M] = 0.8506 mol/L.

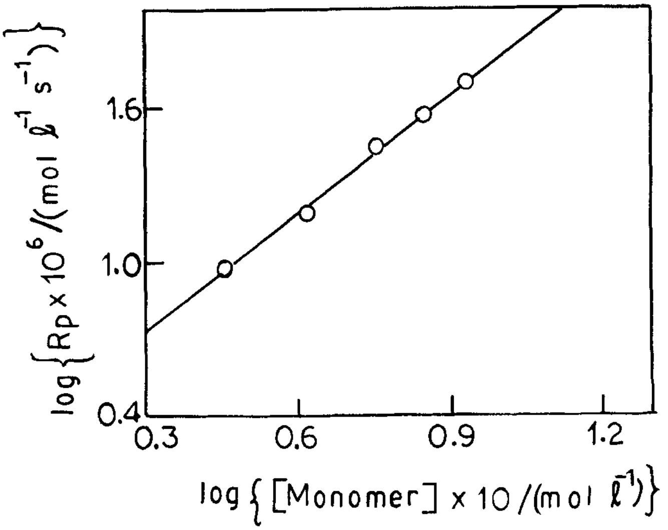

FIG. 4. Relationship between log R_p and log [monomer]. Temperture = 30°C, $[H_2SO_4] = 1.66 \times 10^{-1}$ mol/L, [Ce(IV)] = 8.33×10^{-4} mol/L, [2-propanethiol] = 3.5×10^{-4} mol/L.

TABLE 2. Effect of Hydrogen Ion Concentration on the Rate of Polymerization at 30°C[a]

$[H_2SO_4]$, mol/L	Initial rate, $R_p \times 10^6$, mol/L·s
0.16	50.0
0.13	44.7
0.10	34.7
0.06	26.1

[a] [M] = 0.8506 mol/L, [Ce(IV)] = 8.33×10^{-4} mol/L, [2-propanethiol] = 3.5×10^{-4} mol/L $[SO_4^{2-}]$ = 0.16 mol/L.

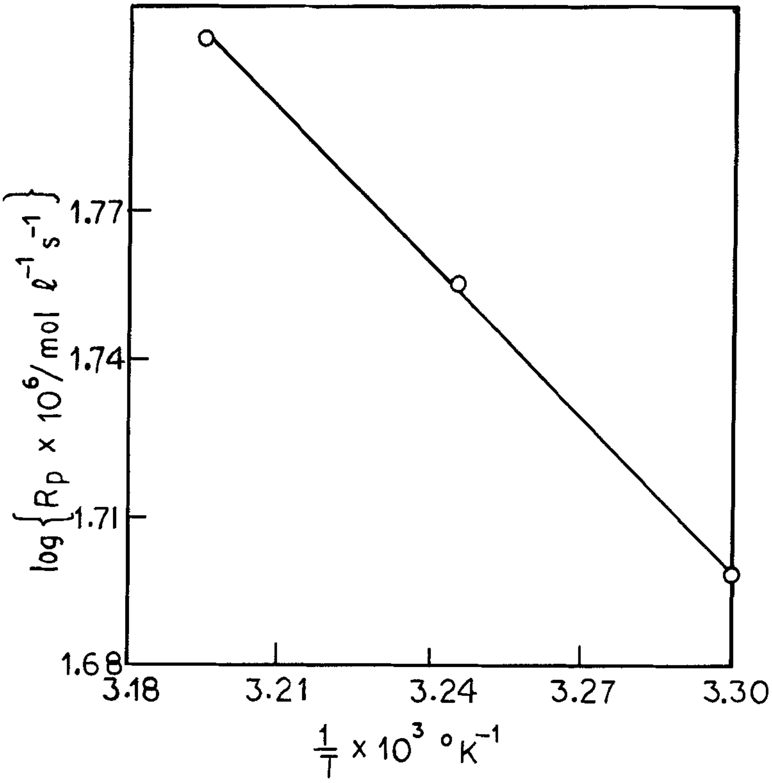

FIG. 5. Dependence of initial rate of polymerization on absolute temperature. [M] = 0.8506 mol/L, [Ce(IV)] = 8.33×10^{-4} mol/L, $[H_2SO_4]$ = 1.66×10^{-1} mol/L, [2-propanethiol] = 3.5×10^{-4} mol/L.

TABLE 3. Dependence of $\overline{DP}$ on Monomer, Thiol, and Ceric Ion Concentrations[a]

[Ce(IV)] × 10^4 mol/L	[M], mol/L	[Thiol] × 10^4 mol/L	$\overline{DP} \times 10^{-4}$	$1/\overline{DP} \times 10^4$
1.66	0.8506	3.50	1.78	0.56
3.33	"	"	1.47	0.68
4.99	"	"	1.23	0.81
6.66	"	"	1.04	0.96
8.33	"	"	0.98	1.02
"	"	2.80	1.10	0.91
"	"	2.10	1.31	0.77
"	"	1.40	1.67	0.60
"	"	0.70	2.22	0.45
"	0.7090	3.50	0.90	1.11
"	0.5670	"	0.77	1.30
"	0.4253	"	0.73	1.36
"	0.2835	"	0.54	1.85

[a] 30°C, $[H_2SO_4] = 1.66 \times 10^{-1}$ mol/L.

the monomer acrylonitrile. The equilibrium constant (K) of the interaction involving complex formation has been evaluated by the well-known procedure of Benesi and Hildebrand [21]. Figure 7 shows the plot of $[C_0]/(A - A_0)$ vs $1/[M]$ according to the expression

$$\frac{[C_0]}{A - A_0} = \frac{1}{K(\epsilon - \epsilon_0)}\,\frac{1}{[M]} + \frac{1}{\epsilon - \epsilon_0} \qquad \text{(A)}$$

where $[C_0]$ is the concentration of Ce(IV); [M] is the concentration of the monomer, acrylonitrile; A_0 is the absorbance of Ce(IV) solution (without the addition of monomer); A is the absorbance in the presence of the monomer; and ϵ_0 and ϵ are the respective molar extraction coefficients in the absence and presence of the monomer. The

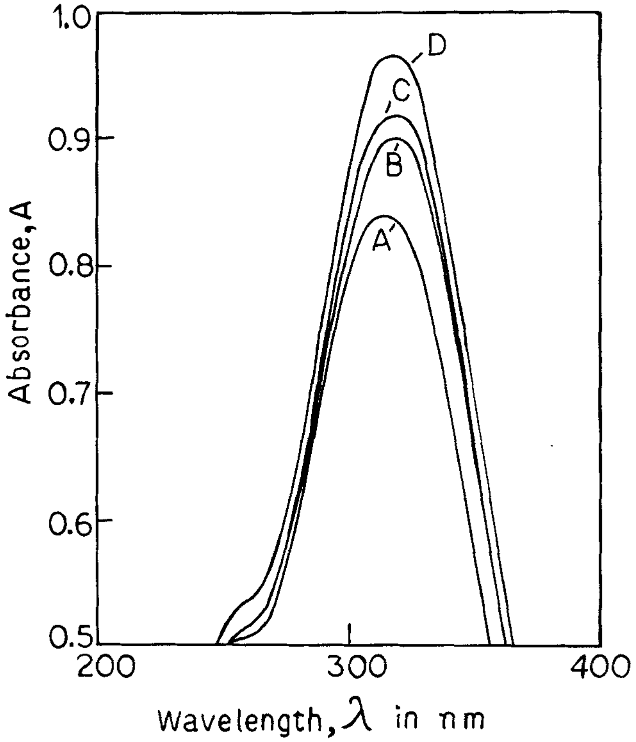

FIG. 6. Plot of wavelength vs absorbance for ceric ammonium sulfate solution in the presence and absence of acrylonitrile. Temperature = 30°C, $[H_2SO_4] = 1.66 \times 10^{-1}$ mol/L, $[Ce(IV)] = 2.5 \times 10^{-4}$ mol/L. (A) [M] = nil, (B) [M] = 0.05 mol/L, (C) [M] = 0.1 mol/L, (D) [M] = 0.2 mol/L.

linearity of the plot indicates 1:1 complex formation, with K = 12.1 L/mol at 30°C (given by the intercept/slope of the plot).

DISCUSSION

The polymerization of acrylonitrile in aqueous medium initiated by ceric ion in the presence of 2-propanethiol shows the usual features of a heterogeneous polymerization. The initially homogeneous reaction system becomes heterogeneous as the polymerization starts due to the insolubility of polyacrylonitrile in the aqueous phase. Autoacceleration in the rate of polymerization is also evident from the reaction curves (Fig. 1). It was generally assumed that autoacceleration

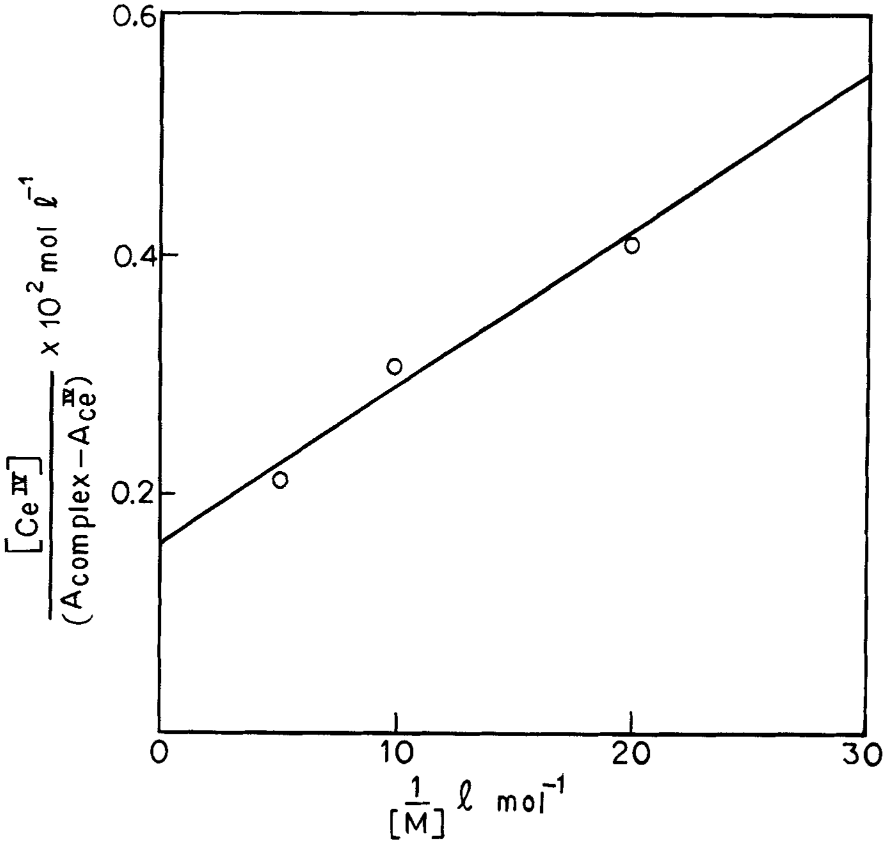

FIG. 7. Plot of $[\mathrm{Ce(IV)}]/(A_{\mathrm{complex}}-A_{\mathrm{Ce(IV)}})$ vs $1/[\mathrm{M}]$. Temperature = 30°C, $[\mathrm{H_2SO_4}] = 1.66 \times 10^{-1}$ mol/L, $[\mathrm{Ce(IV)}] = 2.5 \times 10^{-4}$ mol/L, [M] varies.

was caused by occlusion of growing chains in the precipitated polymer, leading to reduced termination. Recently, however, it was demonstrated [22] that in the case of some polar monomers, e.g., acrylonitrile, there is formed an oriented monomer-polymer association complex (dipole-dipole interaction involving nitrile groups) which favors accelerated propagation and is mainly responsible for the autocatalytic effect observed.

From the experimental results described above, the following mechanism is proposed for polymerization in the present system

$$\mathrm{Ce(IV)} + \mathrm{M} \overset{K}{\rightleftharpoons} \mathrm{B} \tag{1}$$

$$\mathrm{B} + \mathrm{RSH} \xrightarrow{K_d} \mathrm{RS}\cdot + \mathrm{B}' + \mathrm{H}^+ \tag{2}$$

Initiation:

$$\mathrm{RS}\cdot + \mathrm{M} \xrightarrow{k_i} \mathrm{M}\cdot \tag{3}$$

Propagation:

$$\mathrm{M}_n\cdot + \mathrm{M} \xrightarrow{k_p} \mathrm{M}_{n+1}\cdot \tag{4}$$

Transfer:

$$\mathrm{M}_n\cdot + \mathrm{M} \xrightarrow{k_{trM}} \mathrm{M}_n + \mathrm{M}\cdot \tag{5}$$

$$\mathrm{M}_n\cdot + \mathrm{RSH} \xrightarrow{k_{trT}} \mathrm{M}_n\mathrm{H} + \mathrm{RS}\cdot \tag{6}$$

Termination:

$$\mathrm{M}_n\cdot + \mathrm{M}_m\cdot \xrightarrow{k_t} \mathrm{M}_{n+m} \tag{7}$$

Here Ce(IV) is ceric ion or any inorganic complex thereof present in the solution, B is the ceric-monomer complex, RSH is 2-propanethiol, and RS· the thiyl radical formed which initiates polymerization. The species B' may be the cerous form of the complex. The other symbols have the usual meanings. Termination is by mutual interaction of two growing polymer radicals and is indicated by the square-root dependence of the rate on the catalyst concentration. Mutual termination of polymer radicals has also been proposed by Misra et al. in the aqueous polymerization of acrylamide with ceric ion in the presence of thiomalic acid [12] and L-cysteine [13] as initiators.

From the above reaction scheme we get the following expression for the rate of polymerization, R_p, by applying the steady-state principle.

$$R_p = \frac{k_p}{k_t^{1/2}} (k_d Kf)^{1/2} [\mathrm{M}]^{3/2}]\mathrm{Ce(IV)}]^{1/2} [\mathrm{T}]^{1/2} \tag{8}$$

where T represents the thiol and f the initiator efficiency.

The average degree of polymerization $\overline{\mathrm{DP}}$ is given by

$$\frac{1}{\overline{DP}} = C_M + C_T\frac{[T]}{[M]} + \frac{\delta^2}{[M]^2}R_p \tag{9}$$

where C_M ($= k_{trM}/k_p$) and C_T ($= k_{trT}/k_p$) are chain transfer constants with respect to monomer and thiol, respectively, and $\delta = k_t^{1/2}/k_p$.

Thus, the above reaction scheme satisfactorily explains the *kinetic results obtained by us.*

Evaluation of $k_d f$

It can be seen that, if Eq. (8) is valid, the plot of R_p vs $\{[Ce(IV)][T]\}^{1/2}$ at constant monomer concentration should be linear and pass through the origin. Such a plot is shown in Fig. 8. The slope represents $(k_p/k_t^{1/2})(k_dKf)^{1/2}[M]^{3/2}$, according to Eq. (8). Since the values of $k_p/k_t^{1/2}$ ($= 1/\delta$) and K have been determined to be 0.9 (see later) and 12.1 (*from spectroscopic measurements reported earlier*), respectively, at 30°C, and the monomer concentration is known, $k_d f$ can be calculated from the slope and comes out to be 1.34×10^{-3} L/mol·s at 30°C. However, it has not been possible for us to determine the individual values of f and k_d.

Activation Energy

The overall activation energy for the present system, 4.6 kcal/mol (see above), is close to the values observed by Misra and co-workers [13, 23] for the polymerization of acrylamide initiated by Ce(IV)-L-cysteine (4.78 kcal/mol) and Ce(IV)-thioglycollic acid (4.56 kcal/mol) redox systems. Further, from the kinetic expression for R_p (Eq. 8, it can be seen that

$$E_{overall} = E_p + \tfrac{1}{2}E_{k_dK} - \tfrac{1}{2}E_t \tag{10}$$

Values of E_p and E_t for acrylonitrile have been reported by Dainton et al. [24] to be 4.1 and 5.4 kcal/mol, respectively, and the E_{k_dK} calculated by Eq. (10) is 6.4 kcal/mol.

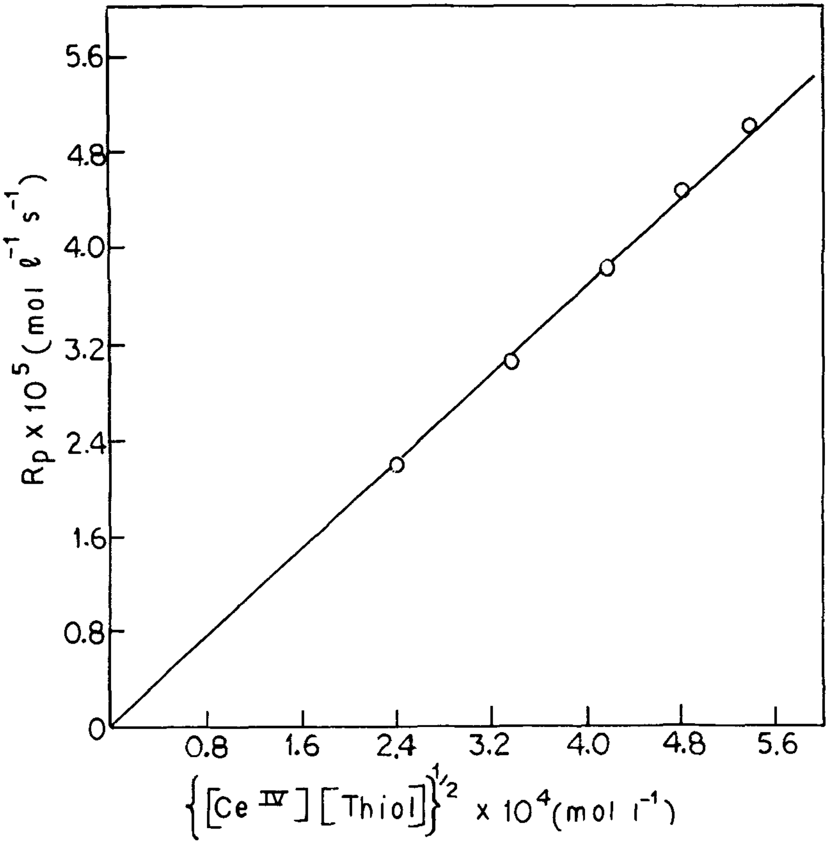

FIG. 8. Relationship between R_p and $\{[Ce(IV)][thiol]\}^{1/2}$. Temperature = 30°C, $[H_2SO_4] = 1.66 \times 10^{-1}$ mol/L, [M] = 0.8506 mol/L.

Effect of H^+ and SO_4^{2-} Ion Concentrations

Tables 1 and 2 show that the rate of polymerization increases with increasing H^+ ion concentration (at constant ionic strength of the medium) whereas it decreases with increasing sulfate ion concentration (at constant hydrogen ion concentration). Similar effects of H^+ ion and sulfate ion concentrations on the rate of polymerization have been observed earlier in this laboratory for acrylonitrile initiated by ceric ammonium sulfate in the presence of organic amines [25], and by Santappa et al. [26] for methyl acrylate and methyl methacrylate initiated by ceric ammonium sulfate-malonic acid. Katai et al. [27]

reported that highly sulfated complexes, which predominate at higher SO_4^{2-} or HSO_4^- and lower H^+ ion concentrations, are less reactive as reactive as regards oxidation of ethylene glycol by Ce(IV). Many other workers [8, 25, 28] concluded from their studies that $Ce(SO_4)_2$ is the active species in the oxidation of thiourea, amines, alcohol, malonic acid, and other substrates by Ce(IV). The results in the present study with Ce(IV)-2-propanethiol are similar to those observed by the above workers, and indicate that $Ce(SO_4)_2$ also is the active species in the present case.

Evaluation of δ, C_M, and C_T

Equation (9) indicates that, provided the monomer and thiol concentrations are kept fixed, plots of $1/\overline{DP}$ vs $[Ce(IV)]^{1/2}$ and $1/\overline{DP}$ vs the corresponding R_p's (Table 3) should be linear. Such plots are shown in Fig. 9. Further, the slope of the $1/\overline{DP}$ vs R_p plot (Fig. 9) represents $(k_t/k_p^2)\ 1/[M]^2$, from which $k_t^{1/2}/k_p = \delta$ can be calculated since [M] is known. The value of δ comes out to be nearly 1.11 at 30°C, somewhat lower ($\simeq 2.04$) than that calculated from the k_p and k_t values as reported by Dainton [24] for the polymerization of acrylonitrile at 30°C, but comparable with the value of about 1.45 at 15°C reported by Ganga Devi and Mahadevan [29]. Widely divergent values of δ have been reported by other workers using different initiator systems. A plausible explanation is that the rate constants involved vary from system to system depending on the heterogeneity of the reaction medium and also on the pH and ionic strength in aqueous systems. Equation (9) further indicates that a plot of

$$\left[\frac{1}{\overline{DP}} - \frac{\delta^2 R_p}{[M]^2}\right] \text{ vs } \frac{[T]}{[M]}$$

should be linear, the slope giving C_T and the intercept C_M. Such a plot for the data in Table 3 is shown in Fig. 10. The value of C_M comes out to be 0.6×10^{-5} at 30°C, which is close to the values of 0.61×10^{-5} and 0.52×10^{-5} obtained by Saha and Chaudhuri [30] in the aqueous polymerization of acrylonitrile initiated by Ce(IV)-amine systems. This also compares favorably with the value 1.05×10^{-5} for C_M at 25°C obtained by Onyon [31] for the bulk polymerization of acrylonitrile. The value of C_T for 2-propanethiol is found to be 0.03 at 30°C. While there is no reported value of C_T for polyacrylonitrile

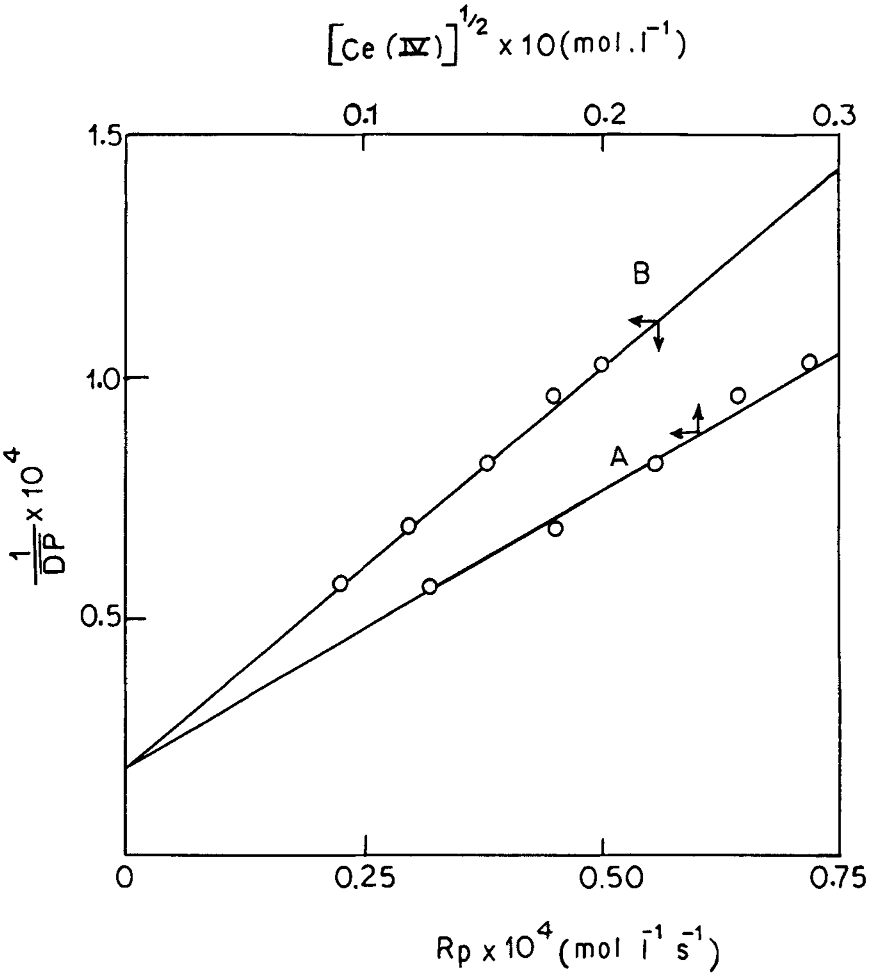

FIG. 9. Dependence of degree of polymerization on (A) ceric ion concentration and (B) corresponding R_p. Temperature = 30°C, [H_2SO_4] = 1.66×10^{-1} mol/L, [M] = 0.8506 mol/L, [2-propanethiol] = 3.5×10^{-4} mol/L, [Ce(IV)] varies.

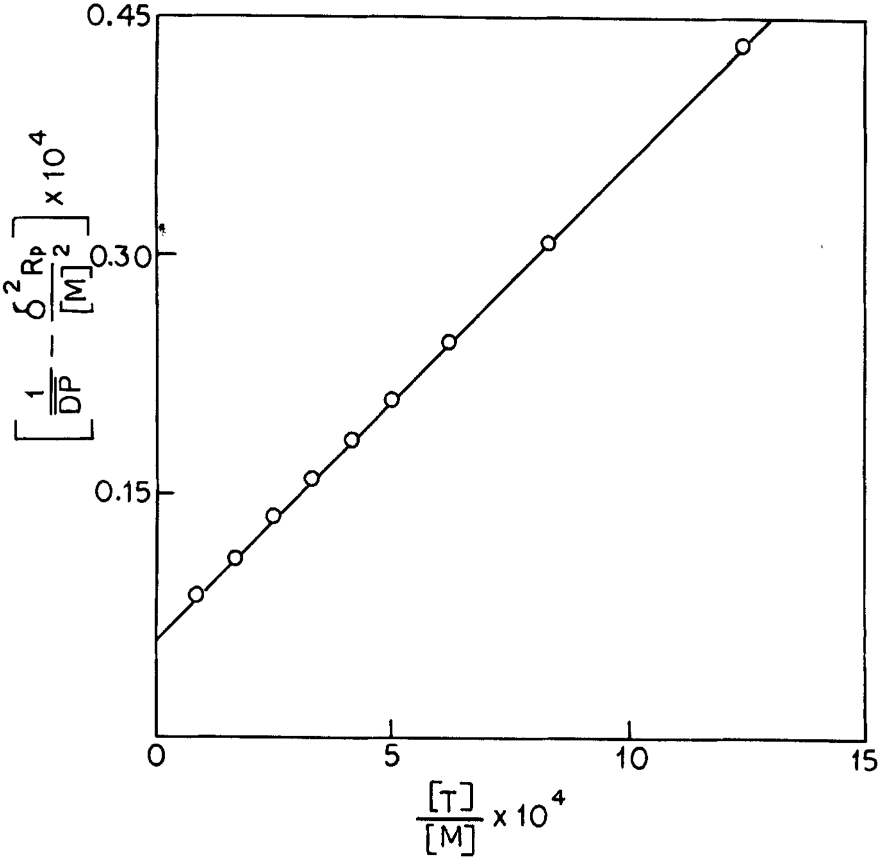

FIG. 10. Plot of $\left[\frac{1}{\overline{DP}} - \frac{\delta^2 R_p}{[M]^2}\right]$ vs [thiol]/[monomer]. Temperature = 30°C, $[H_2SO_4] = 1.66 \times 10^{-1}$ mol/L, $[Ce(IV)] = 8.33 \times 10^{-4}$ mol/L.

radicals with thiols as solvents, this is about 10 times lower than the reported C_T (0.38 at 60°C [32]) for the poly(methyl methacrylate) radical with 2-propanethiol, and more than 100 times lower than those for the polystyrene radical with various thiols. This is in accord with the order expected on the basis of polar contributions to the transition state of the transfer reaction, which will depend on the electron-donating or -accepting properties of the radical [33, 34].

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