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# Aqueous Polymerization of Acrylamide Initiated by Ce(IV)-Thiomalic Acid Redox System

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## SUMMARY

The use of a Ce (IV)-thiomalic acid ($Ce^{4+}$-TMA) redox system as an initiator in the polymerization of acrylamide (M) in an aqueous medium has been investigated. The $Ce^{4+}$ forms a 1:1 complex with TMA, decomposing through free radical mechanism in an acid medium. From 5 to 15% conversion the rate equation is

$$R_p = -\frac{d[M]}{dt} = k[M]^{3/2}[Ce^{4+}]^x[TMA]$$

where $R_p$ is the rate of polymerization and x is 0.5 or 1.0 depending upon the concentration of monomer. The overall energy of activation has been calculated to be 9.12 k cal. $deg^{-1}$ $mol^{-1}$(38.12 kJ/mol) in the investigated range of temperature (25°-40°C) the degree of polymerization (P) of the polymer is directly proportional to [M]. The number of average molecular weight of the polymer remains unaffected at lower concentration of $Ce^{4+}$ and is found to decrease at higher concentrations.

In this investigation the kinetics and mechanism of the Ce(IV)-thiomalic acid (TMA) redox system to initiate the polymerization of acrylamide has been studied.

Acrylamide (E. Merck) was purified by usual methods. Thiomalic acid and ceric ammonium sulfate were used without purification. All solutions were prepared in twice distilled water.

The polymerization procedure adopted was similar to the one used by MISRA et al. [3, 4]. The polymerization was followed by quantitative estimation of the double bonds in acrylamide as described [8]. A small variable induction

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period was observed perhaps due tothe residual oxygen in the thiol solution. Curves were plotted after eliminating the induction period.

The average molecular weights of the polymers were determined by viscosity measurements at 30°C in an aqueous medium using the relationship of DAINTON et al. [2].

$$[\eta]_{30^o} = 6.8 \times 10^{-4}\ \bar{M}n^{0.66}$$

Where $[\eta]$ = intrinsic viscosity of the polymer solution and $\bar{M}n$ = molecular weight of the sample.

## RESULTS

Ceric ammonium sulfate reacts with thiomalic acid to form a yellowish complex which then decomposes slowly in an acid medium (pH 1.3) producing a free radical hydrogen ion and Ce(III). This free radical initiates the polymerization of vinyl monomers. Besides initiating polymerization the primary radicals may undergo dimerization [1] to some extent. It has also been reported by SANTAPPA et al. [7], that probably at higher concentrations of ceric ions the termination of polymerization may be due to ceric ions alone. The mode of termination in the process of polymerization initiated by $Ce^{4+}$ and the organic substrate system has been the subject of controversy. Various workers have postulated various mechanisms. In the present investigation the tentative mechanism may be given as

$$Ce^{4+} + RSH \overset{fast}{\rightleftharpoons} [complex] \xrightarrow{slow} R\dot{S} + Ce^{3+} + H^+ \quad (1)$$

Initiation

$$M + R\dot{S} \longrightarrow \dot{M} \quad (2)$$

Propagation

$$M_{(n-1)} + \dot{M} \longrightarrow \dot{M}n \quad (3)$$

Termination by coupling

$$\dot{M}n + \dot{M}m \longrightarrow \dot{M}(n+m) \quad (4)$$

Termination by $Ce^{4+}$

$$\dot{M}n + Ce^{4+} \longrightarrow Ce^{3+} + H^+ + \text{dead polymer} \quad (5)$$

Dimerization

$$R\dot{S} + \dot{S}R \longrightarrow R\text{-}S\text{-}S\text{-}R \quad (6)$$

RSH represents thiomalic acid, $R\dot{S}$ is the primary radical and M is the monomer. $\dot{M}$ is the radical formed by the reactions of the primary radical with the monomer, and $\dot{M}n$ represents growing polymer radicals. The polymerization of acrylamide alone with Ce$^{4+}$, and complex formation between Ce$^{4+}$ and acrylamide have been reported but seem to be negligible under the present conditions of study. Termination reactions of free radicals take place by coupling. However, the possibility of termination by disproportionation cannot be ruled out altogether.

The complex formed between Ce$^{4+}$ and TMA (step 1) is insoluble in water, methanol, acetone, chloroform and DMF, but it is easily decomposed in a strong acidic medium. It does not melt up to 300$^{0}$C. Conductometric titrations shows complex formation, and the high conductance of the complex at equimolar concentration of metal and ligand indicates that it is an electrolyte. pH measurements show that on adding ligand (TMA) to the fixed amount of Ce$^{4+}$ solution the pH increases gradually. At equimolar concentration a sudden break in the pH is observed, indicating the relation metal: ligand as 1:1. The infrared spectrums of the ligand and the complex were recorded (Table 1).

TABLE 1

IR bands of thiomalic acid and its complex

| Compound | -SH | >C=O of-COOH | C-O str. | C-S | M-O | M-S |
|---|---|---|---|---|---|---|
| TMA | 2550 | 1690 | 1415 | 610 | - | - |
| Complex | - | 1650 | 1400 | 600 | 560 | 480 |

M represents Cerium.

The disappearance of the SH vibration (2550 cm$^{-1}$) in the complex indicates coordination through sulfur. A sharp absorption peak ( C–O ) observed at 1690 cm$^{-1}$ in the ligand shows a shift to 1650 cm$^{-1}$ in the complex. Also the peak of C-O stretching, observed at 1415 cm$^{-1}$ in the ligand, shows a shift to 1400 cm$^{-1}$ in the complex. These changes account for the involvement of the carboxyl group in the complex formation. The C-S stretching frequency (610 cm$^{-1}$) also shows a shift towards lower wave number (600 cm$^{-1}$)

in the complex. The metal-oxygen and metal-sulfur bonds are further confirmed in the far infrared region of the complex, where the two peaks are obtained at 560 and 450 $cm^{-1}$ showing metal-oxygen and metal-sulfur bonding, respectively.

The initial rate of polymerization and the conversion (in mol/l) increases with increasing monomer concentration. The studied range of the monomer concentration is 5.0 x $10^{-2}$ to 3.0 x $10^{-1}$ mol/l at a fixed concentration of $Ce^{4+}$ (5.0 x $10^{-4}$ mol/l) and thiomalic acid (4.0 x $10^{-3}$ mol/l). The rate of polymerization has been found to be proportional to the 3/2 power of the initial monomer concentration. This indicates a bimolecular termination mechanism. The deviation of the exponent from unity to a higher value in the persulfate-initiated polymerization of acrylamide has been explained in terms of a cage effect [6].

The molecular weight of the polymer has been found to increase with increasing concentration of the monomer. A plot of the rate ($R_p$) vs. degree of polymerization ($\bar{P}$) gives a straight line (Fig. 1). Low molecular

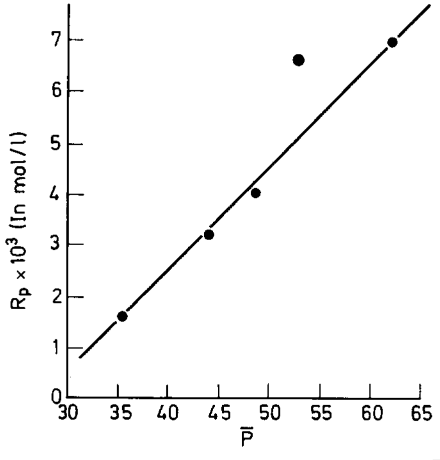

Fig. 1: Plot of the degree of polymerization ($\bar{P}$) vs. the rate of polymerization ($R_p$): [TMA]=4.0 x $10^{-3}$ mol/l, [$Ce^{4+}$] = 5.0 x $10^{-4}$ mol/l, [$H_2SO_4$]= 0.125 mol/l, Temp = 35 ± 0.2°C

weight polymers are obtained here (Table 2).

TABLE 2

Effect of monomer on molecular weight of the polymer $[Ce^{4+}] = 5.0 \times 10^{-4}$ mol/l, [TMA] = 4.0 $10^{-3}$ mol/l, $[H_2SO_4] = 0.125$ mol/l, Temp. = 35 ± 0.2°C.

| Expt. No. | [Monomer]x$10^2$ mol/l | $R_p$x$10^3$ mol/l | Mol. Wt. | Degree of polymerization($\bar{P}$) | $\frac{1}{\bar{P}}$x$10^2$ |
|---|---|---|---|---|---|
| 1. | 10.0 | 1.6 | 2535 | 35.66 | 2.80 |
| 2. | 15.0 | 3.2 | 3158 | 44.43 | 2.25 |
| 3. | 20.0 | 4.0 | 3467 | 48.78 | 2.05 |
| 4. | 25.0 | 6.6 | 3781 | 53.20 | 1.88 |
| 5. | 30.0 | 6.9 | 4445 | 62.54 | 1.60 |

The initial rate of polymerization and the limiting conversion tend to increase with increasing ceric ion concentration at a fixed concentration of monomer, thiomalic acid and sulfuric acid (Fig. 2).

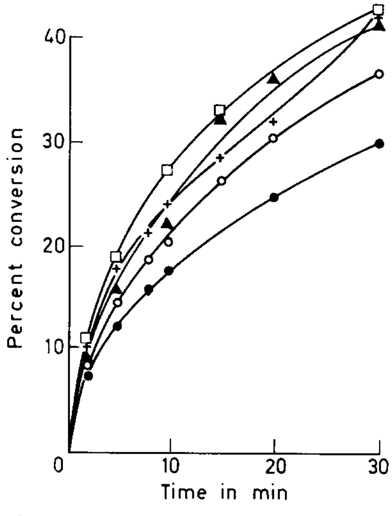

Fig. 2: Time vs. % conversion curves for the aqueous polymerization of acrylamide with varying initial concentrations of $Ce^{4+}$: [Acrylamide]= 5.0 x $10^{-2}$ mol/l, [TMA]= 6.0 x $10^{-3}$ mol/l, $[H_2SO_4]$= 0.125 mol/l, Temp. = 35 ± 0.2°C, (●) $[Ce^{4+}]$= 1.0 x$10^{-3}$ mol/l, (○) $[Ce^{4+}]$=1.25 x $10^{-3}$ mol/l, (▲) $[Ce^{4+}]$ = 1.50 x $10^{-3}$ mol/l, (+) $[Ce^{4+}]$ = 1.75 x $10^{-3}$ mol/l, (◇) $[Ce^{4+}]$ = 2.0 x $10^{-3}$ mol/l.

Two sets of kinetic runs at two concentrations of monomer (5.0 x $10^{-2}$ mol/l and 25.0 x $10^{-2}$ mol/l) were carried out for various initial concentration of $Ce^{4+}$. The concentration ranges of the catalyst in both sets of experiments were approximately similar ($1.0 \times 10^{-3}$ to $2.0 \times 10^{-3}$ and $2.5 \times 10^{-4}$ to $1.5 \times 10^{-3}$ mol/l) and the concentrations of thiomalic acid were $6.0 \times 10^{-3}$ and $4.0 \times 10^{-3}$ mol/l, respectively.

The rate of polymerization showed a half order dependence on the catalyst at the lower monomer concentration and a first order dependence at the higher monomer concentration (Fig. 3).

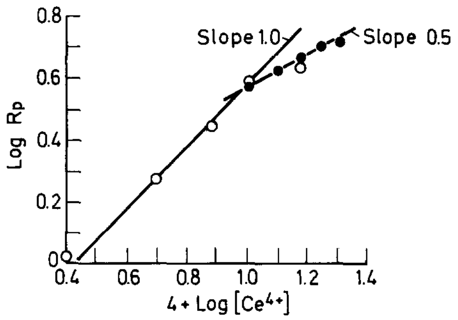

Fig. 3: Double logarithmic plot of the initial rate of polymerization vs. the concentrations of ceric ammonium sulfate in mol/l $[H_2SO_4]$ = 0.125 mol/l, Temp. =35 + 0.2°C (●)[Acrylamide]= $5.0 \times 10^{-2}$ mol/l, [TMA] = $6.0 \times 10^{-3}$ mol/l, (o) [Acrylamide]= $25.0 \times 10^{-2}$ mol/l, [TMA] = $4.0 \times 10^{-3}$ mol/l.

In the presence of oxygen $Ce^{4+}$ alone has been reported to initiate polymerization reactions. However, this was not found in the present investigation.

The exponent 0.5 indicates a bimolecular termination mechanism at lower monomer concentration. But at higher monomer concentration the exponent (1.0) may be due to the termination of the growing chain with ceric ions.

The samples of the polymer for the molecular weight determination were prepared by short stopping the reaction at the point upto which the steady state is observed. The average molecular weight ($\overline{M}n$) of the polymer decreases at higher concentrations of $Ce^{4+}$ and remains unaffected at lower concentrations. Comparatively low molecular weight polymers (formed to some extent) may be due to one of the component thiomalic acids, which is a molecular weight modifier (Table 3).

TABLE 3

Effect of catalyst on molecular weight of the polymer.
[Acrylamide] = 25.0 x $10^{-2}$ mol/l, [TMA] = 4.0 x $10^{-3}$ mol/l
[$H_2SO_4$] = 0.125 mol/l, Temp. = 35 ± 0.2°C

| Expt. No. | [$Ce^{4+}$]x$10^4$ mol/l | $R_p$ | Mol. Wt. | Degree of polymerization($\bar{P}$) | $\frac{1}{\bar{P}}$x$10^2$ |
|---|---|---|---|---|---|
| 1. | 5.0 | 1.9 | 3781 | 53.20 | 1.88 |
| 2. | 7.5 | 2.8 | 3840 | 54.03 | 1.85 |
| 3. | 10.0 | 3.8 | 3763 | 52.94 | 1.89 |
| 4. | 15.0 | 4.3 | 2940 | 41.36 | 2.42 |

The initial rate of polymerization and maximum conversion both increase with increasing concentration of activator(TMA) within the range (2.0 x $10^{-3}$ to 1.0 x $10^{-2}$ mol/l) at a fixed concentration of monomer (5.0 x $10^{-2}$ mol/l) and catalyst (1.0 x $10^{-3}$ mol/l). (Fig. 4).

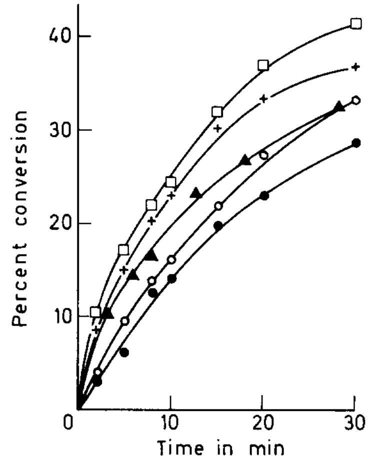

Fig. 4: Time vs. % conversion curves for the aqueous polymerization of acrylamide with varying initial concentration of thiomalic acid (TMA) [Acrylamide]= 5.0 x $10^{-2}$ mol/l, [$Ce^{4+}$]= 1.0 x $10^{-3}$ mol/l, [$H_2SO_4$]= 0.125 mol/l, Temp.=35 ± 0.2°C (●) [TMA]= 2.0 x $10^{-3}$ mol/l, (○) [TMA]= 4.0 x $10^{-3}$ mol/l, (▲) [TMA]= 7.0 x $10^{-3}$ mol/l, (+) [TMA]= 9.0 x $10^{-3}$ mol/l, (□) [TMA] = 1.0 x $10^{-2}$ mol/l.

The order of reaction with respect to the activator has been determined from the double logarithmic plot of $R_p$ vs. the concentration of the activator. The exponent in thiomalic acid is nearly one (1.04). This indicates a first-order dependence of the rate of polymerization on the activator concentration. Similar results have been reported by HUSSAIN et al. [5], in the aqueous polymerization of acrylamide initiated by the potassium persulfate/2-mercaptoethanol redox system. Below a certain concentration ($2.0 \times 10^{-3}$ mol/l) of thiomalic acid no polymerization took place (the concentration of monomer and catalyst were kept constant). This indicates that $Ce^{4+}$ alone does not initiate a polymerization in the studied concentration range.

The effect of temperature has been studied between 25°-45°C. The initial rate, as well as limiting conversion, increases with increasing temperature. Above 40°C the initial rate as well as maximum conversion both were found to decrease probably due to some side reactions. The overall activation energy calculated from the Arrhenius plot was 9.12 k cal. $deg^{-1}$ $mol^{-1}$(38.12 kJ/mol) in the temperature range 20° to 40°C. This is of the same order as the value found in other similar redox systems.

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