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

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To cite this Article Bajpai, U. D. N. and Ahi, Anita(1986) 'Polymerization of Acrylamide Initiated by the Redox System Potassium Persulfate/Lactic Acid, Catalyzed by Silver Ions', Journal of Macromolecular Science, Part A, 23: 3, 305 — 317
To link to this Article: DOI: 10.1080/00222338608063394
URL: http://dx.doi.org/10.1080/00222338608063394

J. MACROMOL. SCI.–CHEM., A23(3), pp. 305-317 (1986)

Polymerization of Acrylamide Initiated by the Redox System Potassium Persulfate/Lactic Acid, Catalyzed by Silver Ions

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ABSTRACT

The aqueous polymerization of acrylamide initiated by the potassium persulfate/lactic acid system catalyzed by Ag^+ ions has been studied iodometrically over the temperature range from 35 to 50 ± 0.2°C. The rate of polymerization is governed by the expression $R_p \propto [M]^{0.8}[K_2S_2O_8]^{1.0}[Ag]^{1.0}$. The deviation from normal kinetics has been studied. A tentative mechanism of initiation is suggested. The overall energy of activation is 5.52 kcal/mol.

INTRODUCTION

α-Hydroxy acids have been used as reductants with a variety of oxidants to bring about vinyl polymerization. Misra et al. [1] have studied the lactic acid/$KMnO_4$ system to polymerize acrylamide. The peroxydisulfate/lactic acid (LA) system has been studied with a view to elucidating the mechanism of free-radical initiation and the kinetic course of the reaction. Since the lactic acid/persulfate ($LA/K_2S_2O_8$) system is very slow, Ag^+ has been used as a catalyst. Peroxydisulfate, when

0022-233X/86/2303-0305$3.50/0

coupled with monovalent silver, acts as a better initiator because Ag^+ is a more powerful oxidant. With hydroxy acids, Ag(II) is formed as a metastable intermediate, bringing about efficient oxidation of the acids. Kern et al. [2] and Whitby et al. [3] have studied the kinetics of polymerization of acrolein initiated by the persulfate/silver redox system. Similar studies have also been done with acrylonitrile [4]. We here report the results of the aqueous polymerization of acrylamide using the Ag^+-catalyzed $K_2S_2O_8$/LA system at 35 ± 0.2°C in a nitrogen atmosphere.

EXPERIMENTAL

Acrylamide (E. Merck, India) was recrystallized twice from methanol (G.R.) and dried in vacuum. Potassium persulfate (A.R.) was used without further purification. Other reagents were of A.R. or equivalent grade. The distilled water was redistilled from a small quantity of alkaline permanganate before use as a solvent.

The polymerization was followed by a quantitative iodometric estimation of double bonds in acrylamide as described by Wallace et al. [5]. The experimental method was the same as described in earlier communications [6]. The conversion was calculated by the formula given by Misra et al. [7]. A short induction period was observed in a few experiments, which may have been due to dissolved oxygen. The graphs were plotted after eliminating the induction period.

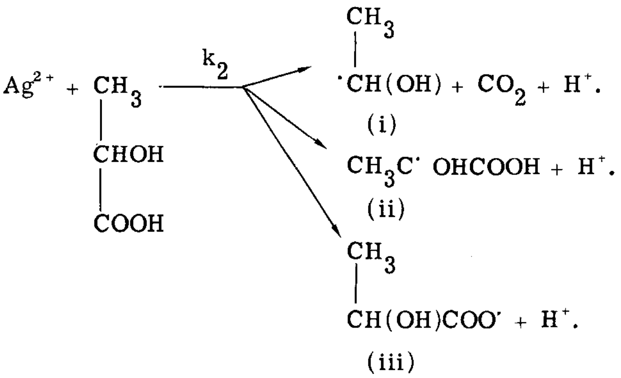
RESULTS AND DISCUSSION

Mechanism and Rate Expression

Persulfate reacts with Ag^+, producing highly reactive Ag^{2+}:

$$Ag^+ + S_2O_8^{2-} \xrightarrow{k_1} Ag^{2+} + SO_4^{\cdot -} + SO_4^{2-} . \qquad (1)$$

The divalent silver reacts with lactic acid, producing free radicals:



$$Ag^{2+} + CH_3CH(OH)COOH \xrightarrow{k_2} \begin{cases} \cdot CH(OH)(CH_3) + CO_2 + H^+. & \text{(i)} \\ CH_3C^{\cdot}OHCOOH + H^+. & \text{(ii)} \\ CH_3CH(OH)COO^{\cdot} + H^+. & \text{(iii)} \end{cases} \qquad (2)$$

In the aliphatic series, reactions such as

$$CH_3CH(OH)COO^{\cdot} \longrightarrow CH_3{}^{\cdot}CHOH + CO_2$$

are very rapid, hence formation of radical (i) ($LA^{\cdot}$) is favored. $LA^{\cdot}$ ($R^{\cdot}$) may initiate polymerization.

$$R^{\cdot} + M \xrightarrow{K_i} R\text{–}M^{\cdot}.$$

$$R\text{–}M^{\cdot} + M \xrightarrow{K_p} R\text{–}M\text{–}M^{\cdot}.$$

$$R\text{–}M\text{–}M^{\cdot} + M \xrightarrow{K_p} M_n^{\cdot}.$$

$$M_n^{\cdot} \xrightarrow{K_t} \text{polymer}.$$

$$LA^{\cdot} + S_2O_8^{2-} \xrightarrow{k_3} CH_3CHO + SO_4^{\bar{\cdot}7} + HSO_4^{-}. \qquad (3)$$

$$\frac{d}{dt}[LA^{\cdot}] = k_2[Ag^{2+}][LA] - k_3[LA^{\cdot}][S_2O_8^{2-}] - K_i[LA^{\cdot}][M] = 0.$$

$$[LA^{\cdot}] = \frac{k_2[Ag^{2+}][LA]}{k_3[S_2O_8^{2-}] + K_i[M]}.$$

When $K_i = K_t$:

$$K_i\,[LA^{\cdot}][M] = K_t[M_n^{\cdot}].$$

$$[M_n^{\cdot}] = \frac{K_i[LA^{\cdot}][M]}{K_t}$$

$$R_p = K_p[M][M_n^{\cdot}],$$

$$= K_p[M]\,\frac{K_i}{K_t}\,[LA^{\cdot}][M],$$

$$= \frac{K_iK_p}{K_t}\,[M]^2\,\frac{k_2[Ag^{2+}][LA]}{k_3[S_2O_8^{\;2-}] + [M]K_i}\,.$$

Now

$$k_1[Ag^+][S_2O_8^{\;2-}] = k_2[Ag^{2+}][LA],$$

or

$$Ag^{2+} = \frac{k_1[Ag^+][S_2O_8^{\;2-}]}{k_2[LA]}\,.$$

Substituting for Ag^{2+}:

$$R_p = \frac{K_iK_p}{K_t}\,[M]^2\,\frac{\dfrac{k_2.k_1[Ag^+][S_2O_8^{\;2-}][LA]}{k_2[LA]}}{k_3[S_2O_8^{\;2-}] + K_i[M]},$$

$$= \frac{K_iK_p}{K_t}\,[M]^2\,\frac{k_1[Ag^+][S_2O_8^{\;2-}]}{k_3[S_2O_8^{\;2-}] + K_i[M]}\,.$$

If $K_i[M] \gg k_3[S_2O_8^{\;2-}]$:

$$R_p = \frac{K_i K_p}{K_t}[M]^2 \frac{k_1[Ag^+][S_2O_8^{2-}]}{K_i[M]},$$

$$= \frac{K_p}{K_t} k_1[M][Ag^+][S_2O_8^{2-}].$$

Dependence of Rate on Redox Components

The initial rate and the maximum conversion tend to increase with increasing persulfate concentration at fixed concentration of lactic acid and acrylamide. It has been seen above that lactic acid or Ag^+ cannot initiate polymerization, and that the reactive species, $LA^\cdot$ and $SO_4^{\cdot-}$, come about by the interaction of persulfate, Ag^+, and lactic acid (Eqs. 1-3). Increasing the persulfate concentration also increases the rate of generation of primary species and hence the initial rate, as well as the maximum conversion. The order with respect to persulfate was determined from the slope of the double logarithmic plot between the initial rate and persulfate concentration (Fig. 1A). The value 1.01 suggests termination by metal ion, or with some impurity present in the system, or chain transfer to solvent molecules.

The initial rate and maximum conversion have been found to increase with increasing lactic acid concentration over a very small range (1.28-2.65×10^{-2} M). At higher concentrations, either the rate is unaffected or shows a retarding effect as the H^+ ion concentration in the system increases.

The effect of excess H^+ ions was also seen by the addition of even a small quantity of H_2SO_4 (5×10^{-4} M) to the system. Retardation of the rate was observed, which gradually increased with increasing H_2SO_4 concentration to 1×10^{-3} M.

An enhancement in the rate of polymerization in a redox system with increasing lactic acid concentration is expected because there is a rise in $LA^\cdot$ free radicals (Eq. 2). However, the effect of excess H^+ ions is to suppress the formation of the active species [8a, 8b]. It supports the results obtained in the presence of excess lactic acid:

$$H^+ + S_2O_8^{2-} \longrightarrow SO_4^{\cdot-} + HSO_4^-,$$

$$H^+ + SO_4^{\cdot-} \longrightarrow HSO_4^-.$$

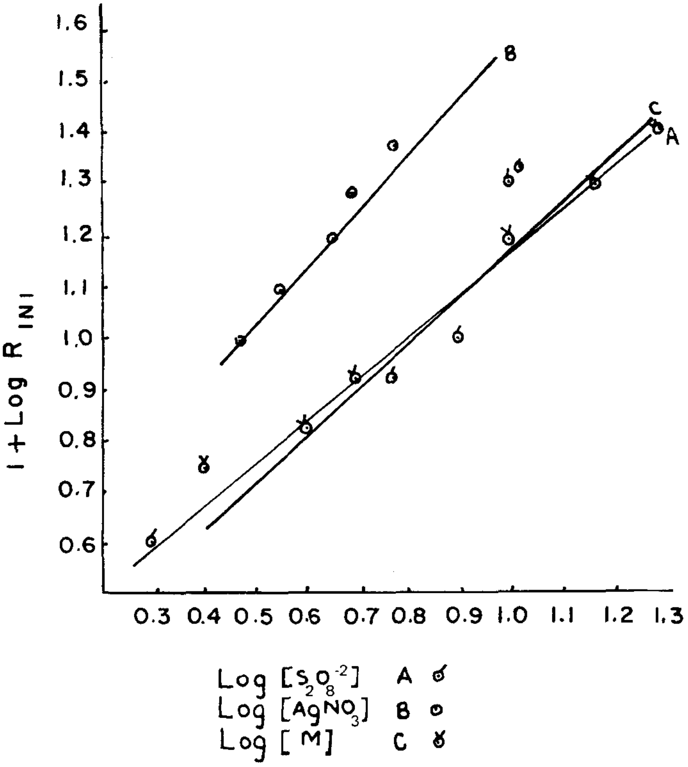


FIG. 1. Double logarithmic plots of initial rate vs log of (A) persulfate concentration, (B) silver nitrate concentration, and (C) monomer concentration.

Effect of Ag^+ Ions

Ag^+ ions play an important part in the process of radical formation. The rate of polymerization and total conversion were found to increase with increasing $[Ag^+]$ in the range $3.0-6.0 \times 10^{-4}$ mol/L. The order with respect to Ag^+ is 1.07 (Fig. 1B). The rate of generation of free radicals (Eqs. 1 and 2) increases with an increase of Ag^+ ions.

Monomer Dependence

The initial rate as well as the percentage conversion increase with increasing monomer concentration (Fig. 2). The rate of polymeriza-

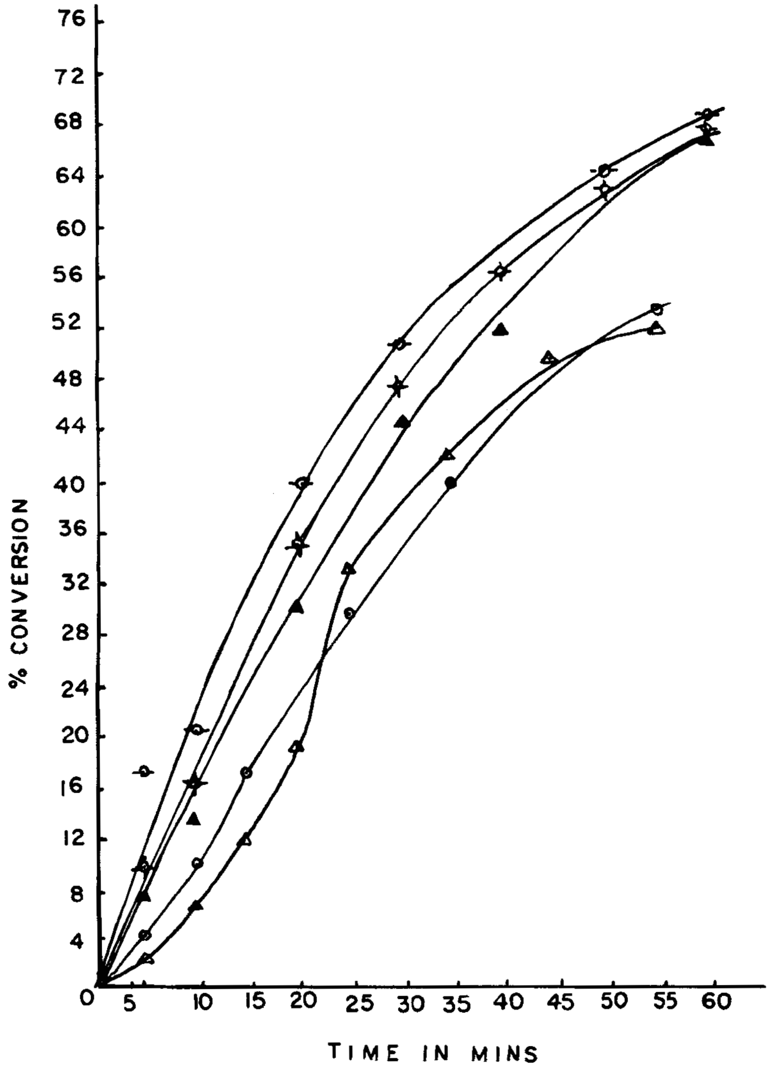


FIG. 2. Time vs conversion curves for the polymerization of acrylamide with varying initial monomer concentration. [Acrylamide] = 5.0×10^{-2} mol/L, [persulfate] = 6.0×10^{-3} mol/L, [silver nitrate] = 3.0×10^{-4} mol/L, [lactic acid] = 2.0×10^{-2} mol/L. 35 ± 0.2°C. Control: ⊙. [M]: 2.5×10^{-2} (△), 10.0×10^{-2} (▲), 15.0×10^{-2} (-✧-), 20.0×10^{-2} (-⊙-).

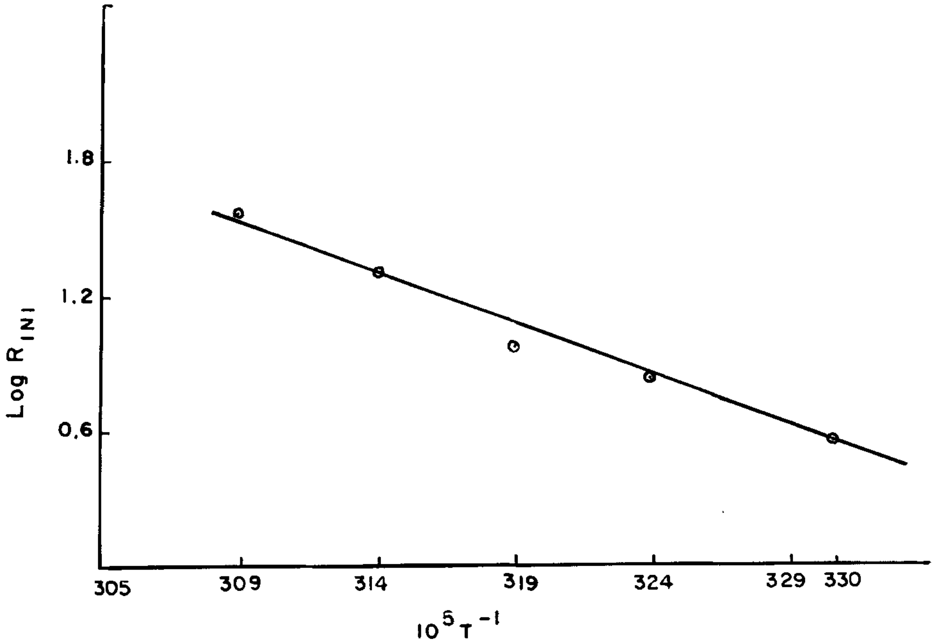


FIG. 3. Arrhenius plot of the initial rate of polymerization (R_{ini}) vs reciprocal of absolute temperature (T) of polymerization.

tion increases linearly with increasing monomer concentration. The monomer exponent was found to be 0.83 (Fig. 1C).

Temperature Dependence

When the temperature of polymerization is raised, the initial rate and the maximum conversion increase. At higher temperatures the rate of generation of active free radicals increases. The overall energy of activation, as calculated from the Arrhenius plot (Fig. 3), is found to be 5.52 kcal/mol within the temperature range from 30 to 50°C. This is of the same order as found in other redox systems [9, 10a, 10b].

Effect of Organic Solvents

Addition of 10% v/v of water-miscible organic solvents (methanol, ethanol, isopropanol, DMF, n-butanol, and dioxane) to the reaction mixture depresses the rate and conversion. Methanol has been found to react with peroxydisulfate [11]:

$$S_2O_8^{2-} + CH_3OH \longrightarrow SO_4^{\cdot -} + HSO_4^{-} + {}^{\cdot}CH_2OH,$$

$$CH_3OH + SO_4^{\cdot -} \longrightarrow HSO_4^{-} + {}^{\cdot}CH_2OH,$$

$${}^{\cdot}CH_2OH + S_2O_8^{2-} \longrightarrow HSO_4^{-} + SO_4^{\cdot -} + CH_2O,$$

$${}^{\cdot}CH_2OH + {}^{\cdot}CH_2OH \longrightarrow CH_3OH + HCHO.$$

The $S_2O_8^{2-}$ is consumed as the reaction with excess methanol occurs, the ${}^{\cdot}CH_2OH$ disproportionates in the process, and the reaction rate falls. Besides this, the retarding effect may also be due to transfer of macroradical chains to the solvent, and the newly formed sluggish solvent radicals may not be capable of initiating polymerization.

When added in equal amounts, the rate of depression in the system is of the order dioxane > n-propanol > butanol > DMF > methanol > ethanol (Fig. 4).

Effect of Inorganic Salts

The addition of small amounts of neutral salts, e.g., $MnSO_4$ and Na_2SO_4, has been found to depress the polymerization rate and maximum conversion (Fig. 5), both possibly due to the resultant increase in the ionic strength of the medium which results in premature termination of the growing polymer chain [12].

$CuSO_4$ brings about an increase in both the rate and the maximum polymerization. The promoting action may be due to some facile reaction path through the intermediacy of the redox system formed by the added metal ion. The rate is found to be retarded on addition of Mn^{2+} because they do not form as efficient a redox system with $K_2S_2O_8$ as with Ag^{2+} and Cu^{+}.

Intermediate Persulfate Injection

Addition of more persulfate to the reaction system after 40 and 50 min brings about an enhancement in the total conversion (Fig. 6). The small amount of catalyst introduced may generate new primary radicals which propagate the reaction at an increased rate.

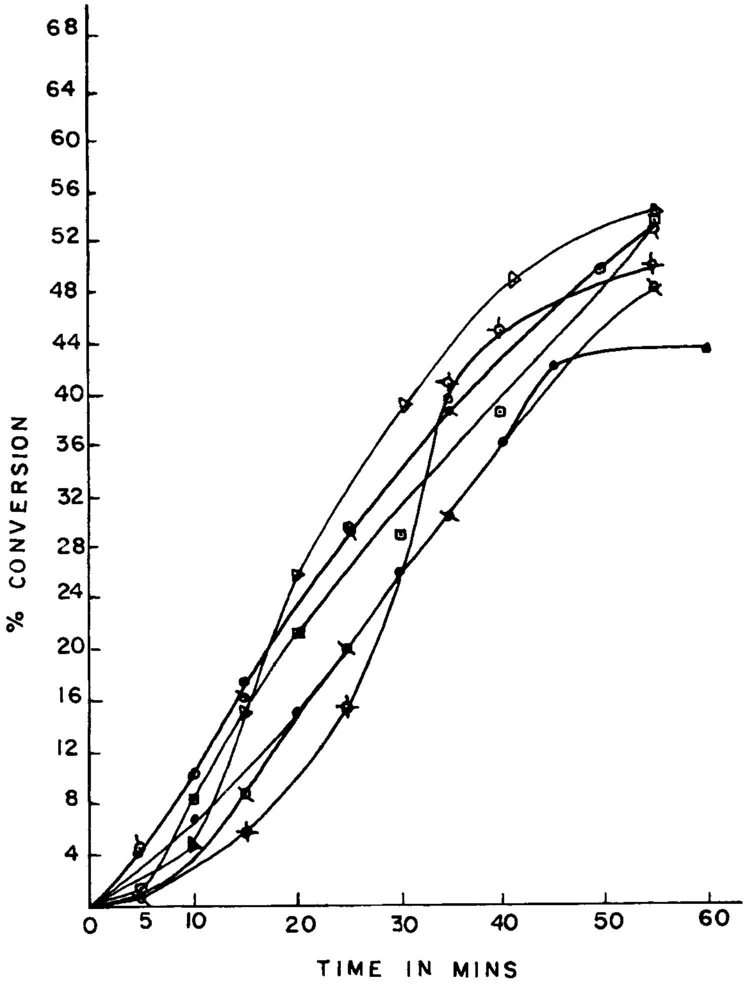


FIG. 4. Effect of addition of water-miscible organic solvents on the polymerization rate of acrylamide. [Acrylamide] = 5.0 × 10^{-2} mol/L, [persulfate] = 6.0 × 10^{-3} mol/L, [silver nitrate] = 3.0 × 10^{-4} mol/L, [lactic acid] = 2.0 × 10^{-2} mol/L. 35 ± 0.2°C. Control: ⊙. Solvents (all 10% v/v): methanol (-⊙-), ethanol (▲), isopropanol (●), butanol (♂), DMF (▣), dioxane (-⌖-).

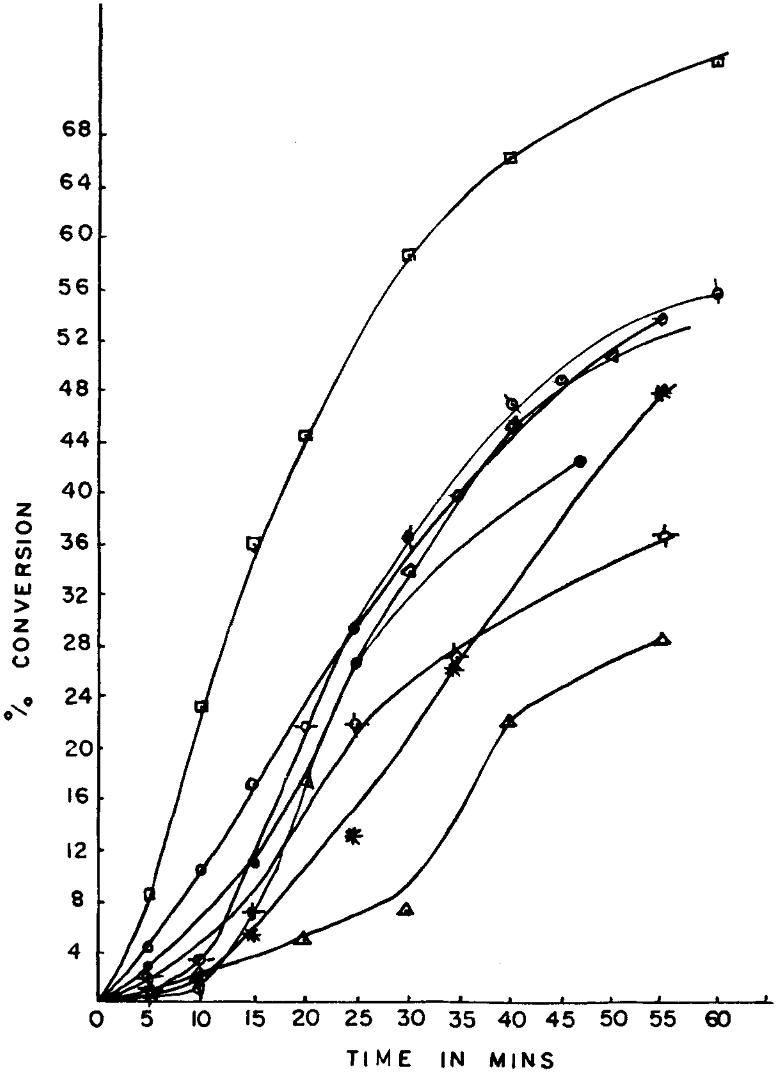


FIG. 5. Effect of addition of inorganic salts and complexing agents on the rate of polymerization of acrylamide. [Acrylamide] = 5.0 × 10^{-2} mol/L, [persulfate] = 6.0 × 10^{-3} mol/L, [silver nitrate] = 3.0 × 10^{-4} mol/L, [lactic acid] = 2.0 × 10^{-2} mol/L. 35 ± 0.2°C. Control: ⊙ [$CuSO_4$], 0.001 M (⊡); [$MnSO_4$], 0.001 M (⊻); [Na_2SO_4], 0.0005 M (-⊙-); [NaF], 0.01 M (-⌽-), 0.02 M (*); [EDTA], 0.0002 M (●), 0.0004 M (▲).

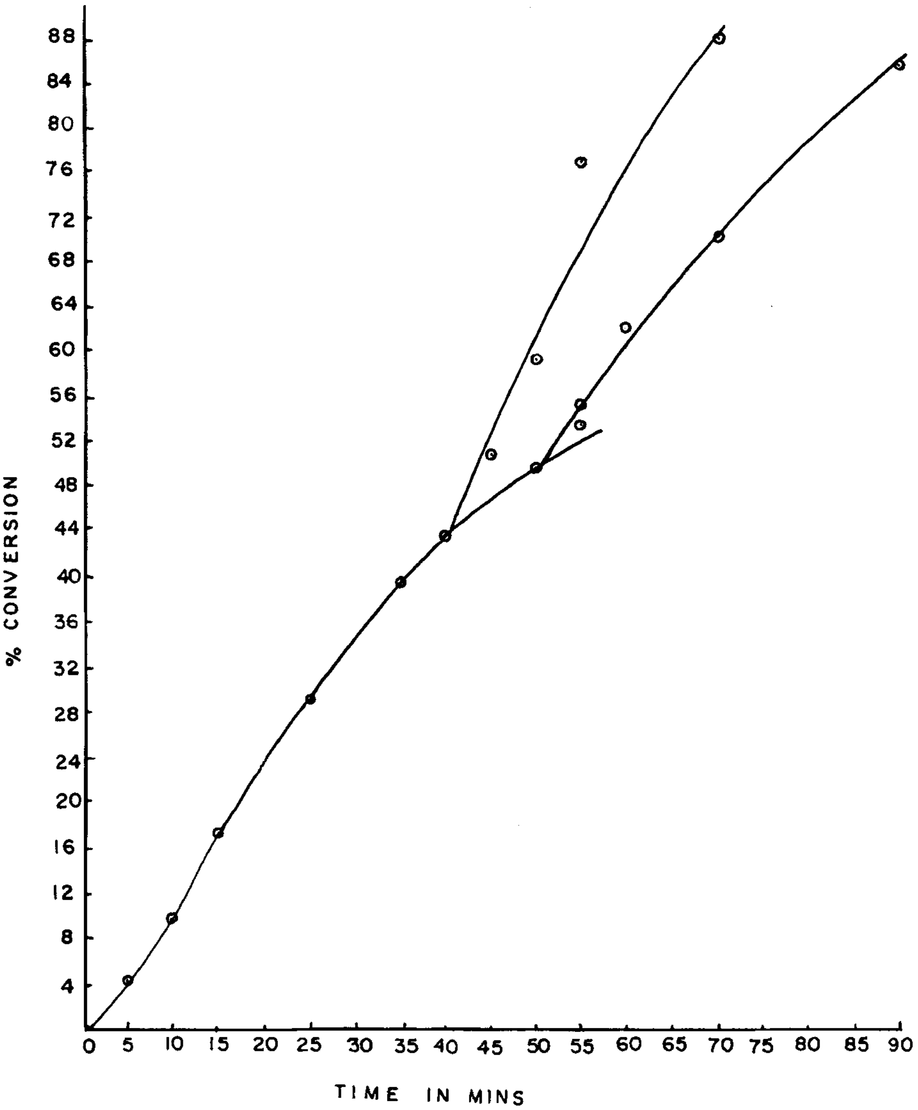


FIG. 6. Effect of injection of further persulfate after 40 and 50 min on the polymerization of acrylamide.

Effect of Complexing Agents

Complexing agents like NaF and EDTA have been found to retard the rate of polymerization and total conversion (Fig. 5). The decrease may be due to formation of a chelate with NaF and complexing with EDTA and Ag^{2+}, thus decreasing the concentration of Ag^{2+}, which is responsible for the generation of primary radicals [8].

ACKNOWLEDGMENT

The authors thank the University Grants Commission (India) for the award of a Junior Research Fellowship to one of them (A.A.).

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Revision received December 15, 1984