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

Permanganate/L-Cysteine Initiated Polymerization of Acrylamide

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To cite this Article Bajpai, U. D. N. and Bajpai, A. K.(1983) 'Permanganate/L-Cysteine Initiated Polymerization of Acrylamide', Journal of Macromolecular Science, Part A, 19: 4, 487 — 500

To link to this Article: DOI: 10.1080/10601328308056530

URL: http://dx.doi.org/10.1080/10601328308056530

J. MACROMOL. SCI.–CHEM., A19(4), pp. 487-500 (1983)

Permanganate/L-Cysteine Initiated Polymerization of Acrylamide

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ABSTRACT

The kinetics of aqueous polymerization of acrylamide with $KMnO_4$/L-cysteine redox system has been studied in an atmosphere of nitrogen at 35 ± 0.2°C. The rate of polymerization has been found to be first power on monomer concentration, 0.5 power with respect to catalyst, and first power with respect to the activator concentration. The overall energy of activation has been calculated to be 11.3 kcal/deg·mol between 30 and 50°C. The effects of various additives (alcohols, neutral salts, complexing agents, surfactants) have also been studied.

INTRODUCTION

Potassium permanganate forms a very effective redox system in the presence of organic reducing reagents such as thioglycolic acid [1], thiomalic acid [2], and thiourea [3] in aqueous acid medium. In the present investigation the $KMnO_4$/L-cysteine redox system has been used to get the low molecular weight polyacrylamide as a highly hydrolyzed low molecular weight polyacrylamide which finds application as a floatation modifier, a suspending agent in the leaching of high solid pulps, etc. As L-cysteine also acts as a modifier, the

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present redox system may throw some light on the superiority of this system over other similar systems in which a modifier is added.

EXPERIMENTAL

Preparation of Materials

Acrylamide was crystallized twice from methanol (A.R.) and dried in vacuum. Potassium permanganate was BDH (Analar) grade. L-cysteine (BDH, England) was used without further purification. Fresh solution was prepared for each run. Other reagents used were of A.R. or equivalent grade. All solutions were prepared in doubly distilled water.

Technique

The polymerization was followed by quantitative estimation of double bonds in acrylamide as described by Wallace et al. [4]. The experimental procedure was similar to that used by Misra et al. [5]. The conversion was calculated with the formula given by Misra et al. [6]. A variable induction period, which may be due to the remaining dissolved oxygen, was observed in some experiments. The graphs were plotted after eliminating the induction period.

RESULTS AND DISCUSSION

Mechanism

Cysteine is known to be oxidized to cystine, and this transformation is proposed to take place through intermediate radical generation. Palit et al. [7] studied the aqueous polymerization of methyl methacrylate using L-cysteine in conjugation with various oxidants such as potassium bromate, persulfate, H_2O_2, and Cu^{2+} as the redox initiator system. They observed the presence of the amino endgroups in polymer chains from their dye partition test. This shows that radical generation takes place by transfer of the labile hydrogen of the sulfydryl group of L-cysteine to the oxidant.

In the present mechanism the transformation of one electron from cysteine to Mn^{4+}, produced by the interaction of acrylamide and permanganate, gives rise to a $RS^{\cdot}$ radical which is assumed to be the chain initiating species. A plausible mechanism is given below to explain the experimental facts. For convenience sake, monomer is denoted by M and L-cysteine as RSH, where R stands for the $-CH_2.CH(COOH).NH_2$ portion of cysteine.

Free Radical Formation:

$$RSH + Mn^{4+} \longrightarrow RS^{\cdot} + Mn^{3+} + H^{+} \tag{1a}$$

$$RSH + Mn^{3+} \longrightarrow RS^{\cdot} + Mn^{2+} + H^{+} \tag{1b}$$

Initiation:

$$RS^{\cdot} + M \longrightarrow M^{\cdot} \tag{2}$$

Propagation:

$$M^{\cdot}_{(n-1)} + M \longrightarrow M_n^{\cdot} \tag{3}$$

Termination by Coupling:

$$M_n^{\cdot} + M_m^{\cdot} \longrightarrow \text{polymer} \tag{4}$$

Termination takes place by mutual interaction of two growing polymer radicals, either by combination or by disproportionation.

Rate Dependence on Redox Components

The initial rate of polymerization and the limiting conversion both increase with increases in the initial concentrations of the activator (L-cysteine) and the catalyst ($KMnO_4$) in the studied range of 1.0 to 9.5×10^{-3} mol/L (Fig. 1a) and 1.2 to 6.0×10^{-3} mol/L (Fig. 2a), respectively, at fixed concentrations of acrylamide (5.0×10^{-2} mol/L) and sulfuric acid (4.5×10^{-3} mol/L).

On increasing the initial concentration of activator, the number of initiating species ($RS^{\cdot}$) increases, which obviously results in an increase in the initial rate of polymerization and limiting conversion. The order of reaction with respect to activator concentration, calculated from the slope of the double logarithmic plot of R_{ini} (in % conversion/min) vs the initial concentrations of activator, has been found to be 1.09 (Fig. 1b), thus showing a first-order dependence of the rate of polymerization on activator concentration. Our results support the work of Hussain et al. [8] who also reported a first-order dependence on activator concentration in $KMnO_4$/thioglycolic acid initiated polymerization of acrylamide. The increase in the initial rate by varying the catalyst concentration may be due to the increase in the rate of production of primary radicals, the number of free radicals, and hence also the number of propagating polymer

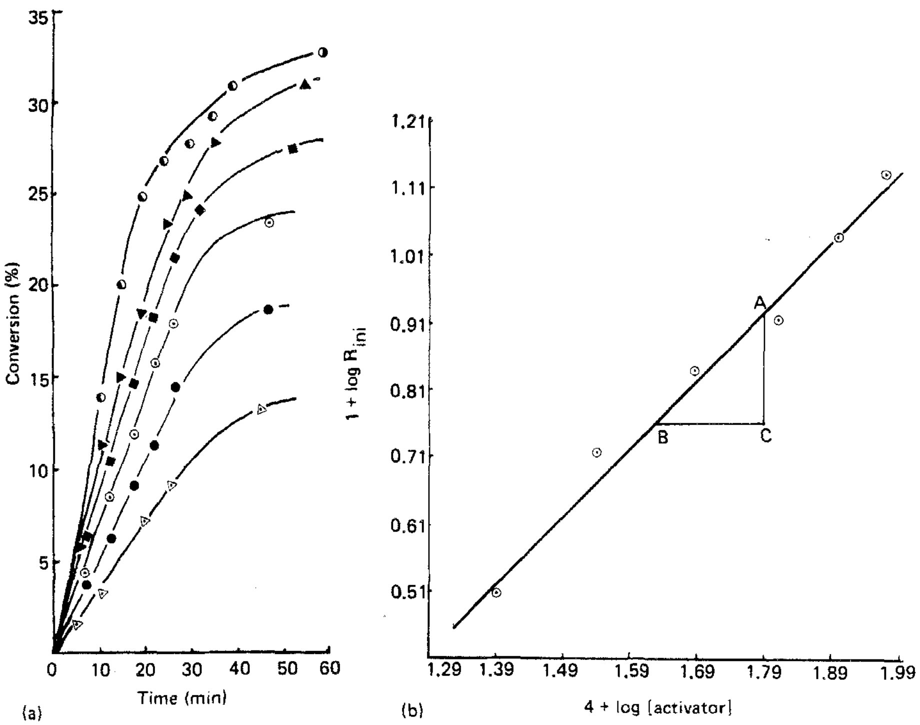


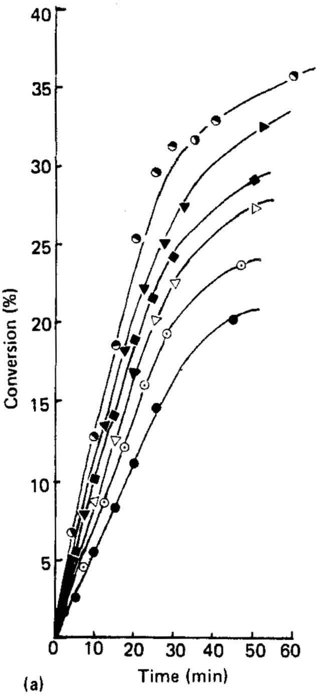
FIG. 1a. Plot of initial course of polymerization of acrylamide for various initial concentrations of L-cysteine (RSH) at fixed $[M] = 5.0 \times 10^{-2}$ mol/L, $[KMnO_4] = 2.0 \times 10^{-3}$ mol/L, $[H^+] = 4.5 \times 10^{-3}$ mol/L, 35 ± 0.2°C. (△) 2.5×10^{-3}, (●) 3.5×10^{-3}, (⊙) 5.0×10^{-3}, (■) 6.5×10^{-3}, (▲) 8.0×10^{-3}, and (◑) 9.5×10^{-3} mol/L.

FIG. 1b. Double logarithmic plot of the initial rate of polymerization (R_{ini} in % conversion per minute) vs the initial concentration of activator (RSH). Slope = 1.09.

radicals. The rate of polymerization has been found to show a normal half-order dependence on the catalyst concentration (Fig. 2b). A half-order dependence on the catalyst confirms a bimolecular chain termination mechanism.

Monomer Dependence

The initial rate of polymerization as well as the limiting conversion were found to increase with the initial concentration of monomer in the range 5.0 to 15.0×10^{-2} mol/L (Fig. 3a). With an increase in



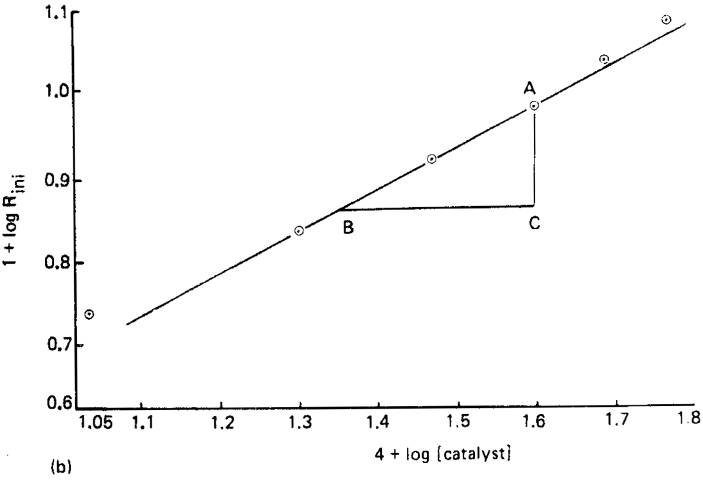
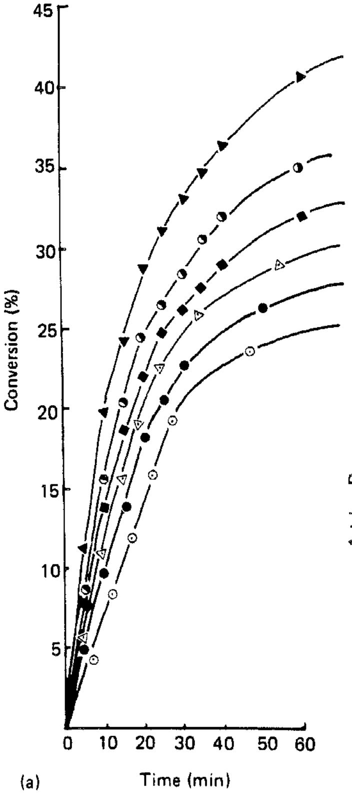


FIG. 2a. Plot of initial course of polymerization of acrylamide for various initial concentrations of $KMnO_4$ at fixed $[M] = 5.0 \times 10^{-2}$ mol/L, $[RSH] = 5.0 \times 10^{-3}$ mol/L, $[H^+] = 4.5 \times 10^{-3}$ mol/L, 35 ± 0.2°C (●) 1.2×10^{-3}, (⊙) 2.0×10^{-3}, (◬) 3.0×10^{-3}, (■) 4.0×10^{-3}, (▲) 5.0×10^{-3}, and (◑) 6.0×10^{-3} mol/L.

FIG. 2b. Double logarithmic plot of the initial rate of polymerization (R_{ini} in % conversion per minute) vs the initial concentration of catalyst ($KMnO_4$). Slope = 0.52.



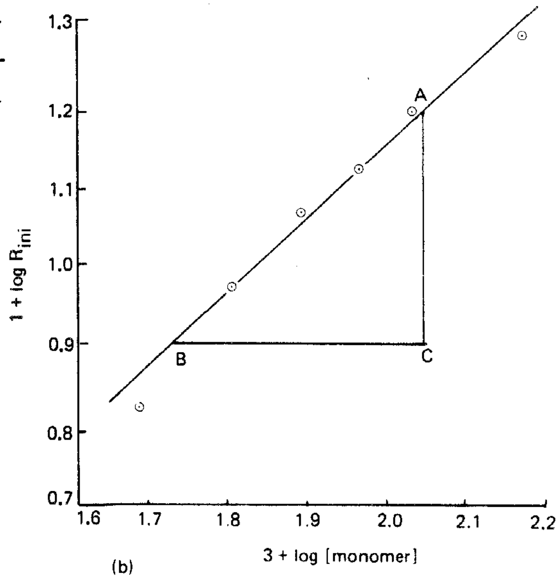


FIG. 3a. Plot of initial course of polymerization of acrylamide for various initial concentrations of monomer at fixed [$KMnO_4$] = 2.0×10^{-3} mol/L, [RSH] = 5.0×10^{-3} mol/L, [H^+] = 4.5×10^{-3} mol/L, 35 ± 0.2°C. (⊙) 5.0×10^{-2}, (●) 6.5×10^{-2}, (△) 8.0×10^{-2}, (■) 9.5×10^{-2}, (◑) 11.0×10^{-2}, and (▲) 15.0×10^{-2} mol/L.

FIG. 3b. Double logarithmic plot of the initial rate of polymerization (R_{ini} in % conversion per minute) vs the initial concentration of monomer. Slope = 0.93.

monomer concentration, the availability of monomer molecules in the propagation step increases, resulting in an increase in the rate of polymerization. The value of the monomer exponent has been found to be 0.93 (Fig. 3b), thereby confirming the first power dependence of the rate on monomer concentration as is usually observed in redox polymerization. Several workers [9, 10] have reported a general deviation from linearity at a higher concentration of monomer

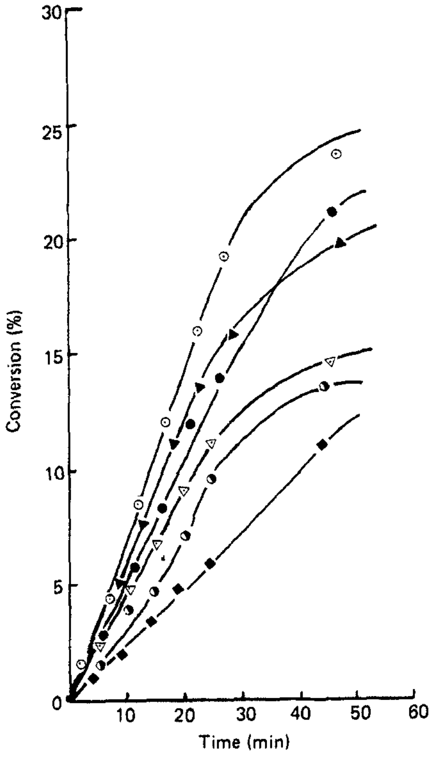


FIG. 4. Plot of initial course of polymerization of acrylamide for various initial concentrations of $H_2SO_4(H^+)$ at fixed [M] = 5.0×10^{-2} mol/L, [$KMnO_4$] = 2.0×10^{-3} mol/L, [RSH] = 5.0×10^{-3} mol/L, 35 ± 0.2°C. (■) 1.0×10^{-3}, (◑) 1.8×10^{-3}, (◬) 2.7×10^{-3}, (●) 3.6×10^{-3}, (◉) 4.5×10^{-3}, and (▲) 5.4×10^{-3} mol/L.

because of the increased viscosity of the reaction medium; however, no such deviation from linearity has been observed in the present study.

Effect of Sulfuric Acid

Marginal increases in the initial rate and limiting conversion has been observed with an increase in the acid concentration in the range of 1.0 to 4.5×10^{-3} mol/L. On further increasing the acid concentration ($> 4.5 \times 10^{-3}$ mol/L) a decrease in limiting conversion has been observed (Fig. 4). The increase in initial rate and limiting conversion may be explained as follows.

In systems containing thiol as one of the components, the following equilibrium generally becomes significant in aqueous medium:

$$RSH \rightleftharpoons RS^- + H^+ \qquad (5)$$

The reactive form of thiol in initiating polymerization is RSH and not RS^-. Benesch and Benesch [11] have reported that cysteine slightly dissociates into the sulfide form RS^- in highly acid medium. Thus, with an increase in sulfuric acid (H^+ ions) concentration in the reaction medium, the concentration of undissociated thiol, i.e., RSH, increases (Eq. 5); consequently, the rate of polymerization increases. At a higher concentration of H^+ ions in the reaction medium, H^+ ions reduce Mn^{4+} ions to Mn^{2+} ions and liberate the inhibiting oxygen according to the side reaction

$$MnO_2 + 2H^+ \longrightarrow Mn^{2+} + H_2O + O \qquad (6)$$

Thus the rate of generation and the concentrations of reactive species are suppressed. This results in a decrease in the rate and limiting conversion.

Temperature Dependence

The effect of temperature on the polymerization rate has been studied in the range of 30 to 50°C. The initial rate and limiting conversion increase with an increase in the temperature (Fig. 5a). The overall energy of activation as calculated from an Arrhenius plot (Fig. 5b) has been found to be 11.3 kcal/deg·mol within the temperature range of 30 to 50°C. This value is of the same order as is found in similar redox systems.

EFFECT OF ADDITIVES

Effect of Organic Solvents

Water miscible organic solvents (methanol, ethanol, DMF, dioxane, n-propanol, n-butanol) all depress the rate as well as the limiting conversion (Fig. 6a). This is probably caused by a decrease in the area of shielding of a strong hydration layer in the aqueous medium, resulting in termination of the radical end of the growing chain, or the increase in the regulated rate of production of primary radicals caused by the solvent, which under the studied experimental conditions renders the termination rate relatively fast as compared to the rate of the propagation step, as pointed out by Kern et al. [12]. The

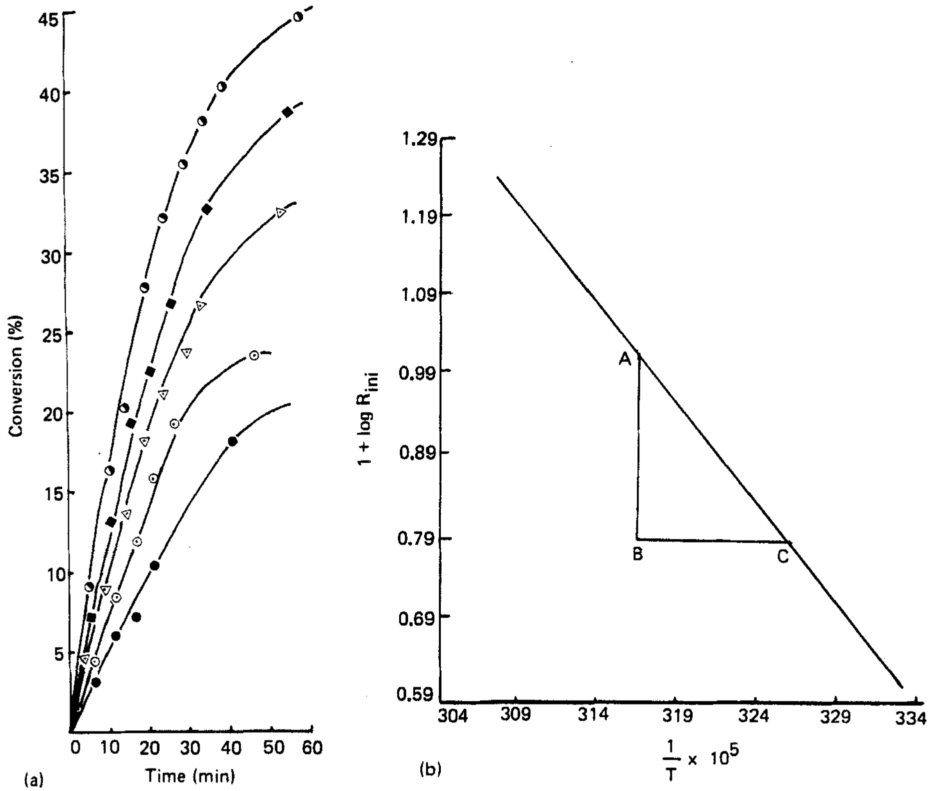


FIG. 5a. Plot of initial course of polymerization of acrylamide at varying temperatures at fixed [M] = 5.0×10^{-2} mol/L, [KMnO$_4$] = 2.0×10^{-3} mol/L, [RSH] = 5.0×10^{-3} mol/L, [H$^+$] = 4.5×10^{-3} mol/L. (●) 30, (⊙) 35, (△) 40, (■) 45, and (◑) 50°C.

Fig. 5b. Arrhenius plot. [M] = 5.0×10^{-2} mol/L, [KMnO$_4$] = 2.0×10^{-3} mol/L, [RSH] = 5.0×10^{-3} mol/L, [H$^+$] = 4.5×10^{-3} mol/L. Energy of activation E_a = 11.3 kcal/deg•mol.

interchain hydrogen bonding interlocking the polymer chain is not rigid, which also causes the premature mutual combination of the polymer chains.

When added in equal quantity (5% v/v), the order of depression of the rate of polymerization and the induction period increases: dioxane < MeOH < EtOH < n-propanol < n-butanol < DMF.

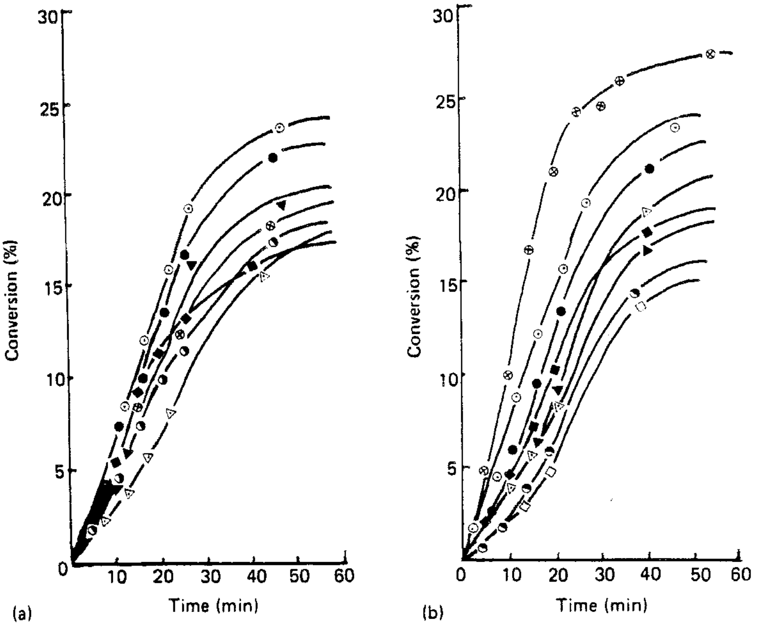


FIG. 6a. Plot of initial course of polymerization of acrylamide in various media at fixed [M] = 5.0 × 10^{-2} mol/L, [$KMnO_4$] = 2.0 × 10^{-3} mol/L, [RSH] = 2.0 × 10^{-3} mol/L, [H^+] = 4.5 × 10^{-3} mol/L, 35 ± 0.2°C. (◬) n-butanol (5% v/v), (◑) n-propanol (5% v/v), (⊕) ethanol (5% v/v), (▲) methanol (5% v/v), (■) DMV (5% v/v), (●) dioxane (5% v/v), (⊙) H_2O medium.

FIG. 6b. Effect of cations on the plot of initial course of polymerization of acrylamide for varying concentrations of various salts added at fixed [M] = 5.0 × 10^{-2} mol/L, [$KMnO_4$] = 2.0 × 10^{-3} mol/L, [RSH] = 5.0 × 10^{-3} mol/L, [H^+] 4.5 × 10^{-3} mol/L, 35 ± 0.2°C. (▣) K_2SO_4 = 0.02, (◑) Na_2SO_4 = 0.02, (▲) K_2SO_4 = 0.01, (◬) Li_2SO_4 = 0.02, (■) Na_2SO_4 = 0.01, (●) Li_2SO_4 = 0.01, (⊕) $MnSO_4$ = 0.02 mol/L, and (⊙) no salt added.

Effect of Addition of Salts and Complexing Agents

The effect of various neutral salts on the rate of polymerization has also been investigated. In every case except with $MnSO_4$ the rate and the limiting conversion were found to decrease. This decrease is proportional to the amount of the salt added and the basicity of the salt. The rate of depression is of the order (Fig. 6b) K_2SO_4 > Na_2SO_4 > Li_2SO_4.

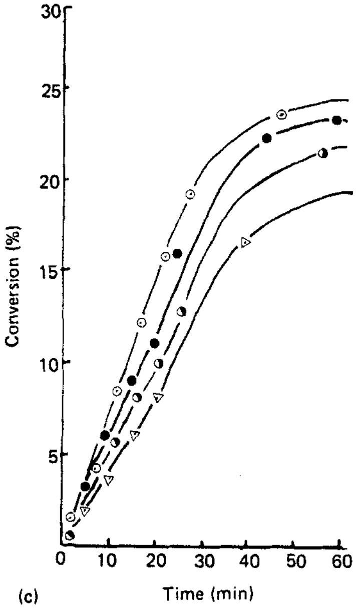


FIG. 6c. Effect of anions on the plot of initial course of polymerization of acrylamide for varying concentrations of various salts added at fixed [M] = 5.0 × 10^{-2} mol/L, [$KMnO_4$] = 2.0 × 10^{-3} mol/L, [RSH] = 5.0 × 10^{-3} mol/L, [H^+] = 4.5 × 10^{-3} mol/L, 35 ± 0.2°C. (△) K_2SO_4 = 0.01, (◑) KBr = 0.01, (●) KCl = 0.01 mol/L, and (⊙) no salt added.

When the anions were different, the order of depression of rate was found to increase as follows (Fig. 6c): K_2SO_4 > KBr > KCl.

The depression in the rate and in limiting conversion might be due to the ionic dissociation of the added electrolytes which interfere with the usual polymerization reaction, resulting in the premature termination of the growing polymer chains and a large reduction of the activity of the Mn^{4+}/Mn^{3+} ions due to ion coupling with the added salts.

An increase in rate and limiting conversion due to the introduction of manganous sulfate has been found which can be explained in accordance with the suggestion made by Palit et al. [13] that a disproportionation reaction occurs between the Mn^{2+} and Mn^{4+} ions, producing the highly active Mn^{3+} ions in the system at a rapid rate. The trivalent manganese ions thus formed react rapidly with the organic substrate (Eq. 1b) in solution, producing free radicals which propagate the polymerization reaction at a comparatively faster rate.

Both NaF and EDTA depress the rate of polymerization and the limiting conversion, and the induction period increases slightly

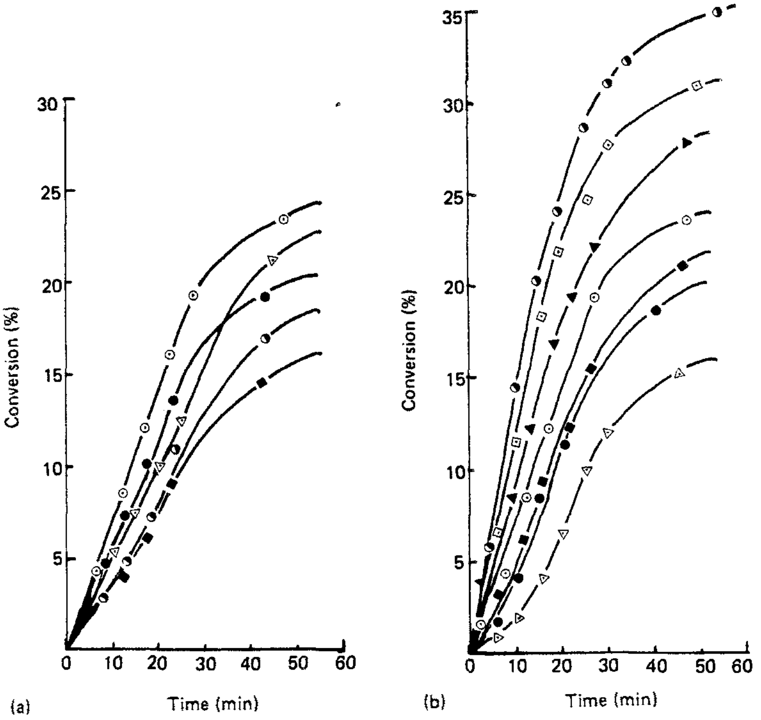


FIG. 7a. Effect of complexing agents on the plot of initial course of polymerization of acrylamide for varying concentrations of various salts added at fixed [M] = 5.0×10^{-2} mol/L, [$KMnO_4$] = 2.0×10^{-3} mol/L, [RSH] = 5.0×10^{-3} mol/L, [H^+] = 4.5×10^{-3} mol/L, 35 ± 0.2°C. (■) NaF = 0.02, (◑) EDTA = 0.02, (●) EDTA = 0.01, (△) NaF = 0.01 mol/L, and (⊙) no salt added.

Fig. 7b. Effect of surfactants on the plot of initial course of polymerization of acrylamide for varying concentrations of various surfactants added at fixed [M] = 5.10×10^{-2} mol/L, [$KMnO_4$] = 2.0 $\times 10^{-3}$ mol/L, [RSH] = 5.0×10^{-3} mol/L, [H^+] = 4.5×10^{-3} mol/L, 35 ± 0.2°C. (△) CTAB = 1.64×10^{-3}, (●) CTAB = 0.82×10^{-3}, (■) CTAB = 0.1×10^{-3}, (▲) sodium oleate = 0.05×10^{-4}, (⊡) sodium oleate = 0.1×10^{-4}, (◑) sodium oleate = 0.2×10^{-4} mol/L, and (⊙) no surfactant added.

(Fig. 7a). The depression caused by NaF may be explained in terms of its complex formation between the Mn^{3+} initially formed and fluoride ions, thus bringing about an appreciable suppression of the rate of production of free radicals and thereby decreasing the rate. Palit et al. [14] have reported a depression in the initial rate but an

TABLE 1

No.	Surfactant used	Hydro carbon chain length	Concentration (mol/L) × 10^3	CMC (mol/L) × 10^3	Effect on the rate of polymerization, R_p
1	Cetyl trimethyl ammonium bromide CTAB (cationic)	C_{16}	0.1-1.64	0.82	Decreased below and above CMC
2	Sodium oleate (anionic)	C_{18}	0.1-0.2	0.05	Increased below and above CMC

enhancement in the limiting conversion by the addition of NaF due to the formation of the complex first and then its decomposition at a later stage. Shukla et al. [15] reported an increase in both the initial rate and limiting conversion in the aqueous polymerization of acrylamide initiated by the $KMnO_4$/ascorbic acid system. In our experimental conditions, this type of result is not prominent.

The effect of EDTA may be attributed to its chelating characteristics and the stability of the chelate with Mn^{4+} ions of the MnO_2. The Mn^{4+} ions are thus prevented from oxidizing L-cysteine and thereby decreasing the rate.

Effect of Surfactants

The influence of surfactants on the rate of polymerization is summarized in Fig. 7b and Table 1. The rate of polymerization and the limiting conversion both appear to increase in the presence of the anionic surfactant, sodium oleate, which may be due to a decrease in H^+ ions due to their absorption on the surface of the anionic micelles, thereby decreasing the possibility of side reactions (Eq. 6). The coulombic repulsion is also minimized, and therefore an increase in the rate of polymerization and in limiting conversion is observed. Similar results were also reported by other workers in the presence of other anionic active surfactants (Jadinol PU [15], Cetevelon [14], and sodium cetyl sulfate [13]) in redox polymerization.

Furthermore, the rate was found to decrease in the presence of cationic surfactant cetyl trimethyl ammonium bromide (CTAB) below, at, and above its CMC value. This may be explained by assuming specific ion pair binding of the large anion MnO_4^- with the large cation R_4N^+ which may lower the rate of primary radical generation. Alexender et al. [16] have reported such ion pair binding above the

CMC, leading to the formation of an insoluble complex which could be dispersed by further addition of cationics. Hence the rate is reduced. Our study finds support from earlier workers [15, 17].

ACKNOWLEDGMENT

The authors desire to thank CSIR, New Delhi, India, for financial assistance to one of them (A.K.B.).

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Accepted by editor June 12, 1982
Received for publication July 12, 1982