degradation is now being studied.

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Registry No. $TaCl_5$, 7721-01-9; Me_4Sn, 594-27-4; Et_4Si, 631-36-7; Bu_3SnH, 688-73-3; Bu_3SnCl, 1461-22-9; Ph_3SnCl, 639-58-7; Ph_3SiH, 789-25-3; Ph_4Sn, 595-90-4; Ph_3Sb, 603-36-1; BuLi, 109-72-8; *t*-BuLi, 594-19-4; Ph_3B, 960-71-4; $NbCl_5$, 10026-12-7; Bu_4Sn, 1461-25-2; Et_3SiH, 617-86-7; Ph_3Bi, 603-33-8; 9BBN, 280-64-8; poly(1-phenyl-1-propyne), 53621-07-1; sodium bis(2-methoxyethoxy)aluminum hydride, 22722-98-1.

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(8) The time course for intrinsic viscosity was reported.[2] Here the time–$\bar{M}_w$ relationship is shown to help understand the present degradation.
(9) Since the time when 100% conversion is reached is more or less irreproducible owing to trace amounts of water in the system, it is not necessarily easy to prepare a high-molecular-weight poly(1-phenyl-1-propyne) with $TaCl_5$ alone.
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Aqueous Polymerization of Acrylamide Initiated with the Permanganate–L-Serine Redox System

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ABSTRACT: The effect of various parameters, salts, organic solvents, and temperature on the rate of polymerization of acrylamide initiated by permanganate–L-serine, a new redox system, has kinetically been studied in an inert atmosphere of nitrogen at 35 ± 0.2 °C. Variation in molecular weight of polyacrylamide at varying initial concentration of monomer has also been studied.

Introduction

L-Serine has been used as a reductant in kinetic studies of reduction of Ce(IV), Fenton's reagent, and chloramine-T,[1-3] but its use as an activator in radical polymerization has not been investigated so far. In the present study it is being used, for the first time, as an activator in the polymerization of acrylamide, with potassium permanganate as a catalyst. L-Serine itself finds applications as a vulcanizing accelerator for diene rubber and as a chemical modifier for silk and wool fibers. We have studied in our laboratory permanganate–L-cysteine[4] and permanganate–glycine[5] initiated polymerization of acrylamide. In the same series, we are reporting the results of permanganate–L-serine initiated polymerization of acrylamide.

Experimental Section

Acrylamide was recrystallized twice from methanol (AR) followed by drying under vacuum. Potassium permanganate used was BDH (AnalaR) grade, and its solution was prepared by a standard method.[6] All solutions were prepared in double-distilled water. The apparatus and procedure employed were identical with those used by Misra et al.[7] in which the kinetics of polymerization was followed by estimating the rate of consumption of monomer.

The molecular weight of polyacrylamide was determined by viscometry with Suen's equation[8]

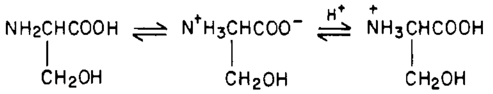
$$[\eta]_{\text{spc}} = 6.8 \times 10^{-4} M^{0.66}$$

Results and Discussion

Mechanism. The free radicals, which are responsible for the initiation of polymerization, are produced by the redox reaction between L-serine and potassium permanganate. A plausible mechanism suggested for the present study may be outlined as follows:

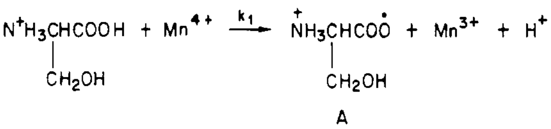
(a) Formation of Free Radicals

In general, L-serine exists predominantly as the protonated species in acidic media according to the equation

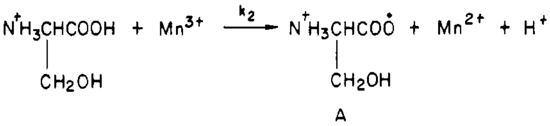


$$\underset{CH_2OH}{NH_2CHCOOH} \rightleftharpoons \underset{CH_2OH}{N^+H_3CHCOO^-} \overset{H^+}{\rightleftharpoons} \underset{CH_2OH}{\overset{+}{N}H_3CHCOOH} \quad (1)$$

In permanganate-containing redox systems, first the permanganate reacts with acrylamide to produce manganese dioxide, which in acidic medium combines with protonated L-serine to yield free radicals A and B (eq 2–4).



$$\underset{CH_2OH}{N^+H_3CHCOOH} + Mn^{4+} \xrightarrow{k_1} \underset{\underset{A}{CH_2OH}}{\overset{+}{N}H_3CHCO\dot{O}} + Mn^{3+} + H^+ \quad (2)$$



$$\underset{CH_2OH}{\overset{+}{N}H_3CHCOOH} + Mn^{3+} \xrightarrow{k_2} \underset{\underset{A}{CH_2OH}}{N^+H_3CHCO\dot{O}} + Mn^{2+} + H^+ \quad (3)$$

The MnO_2-controlled initiation (eq 2) has been confirmed by the addition of fresh MnO_2 to the reaction medium, which increases the initial rate of polymerization and maximum conversion as well.

The free radical A produced above now decomposes as follows:

$$A \xrightarrow[\text{fast}]{k_3} \underset{B}{N^+H_3\dot{C}HCH_2OH} + CO_2 \quad (4)$$

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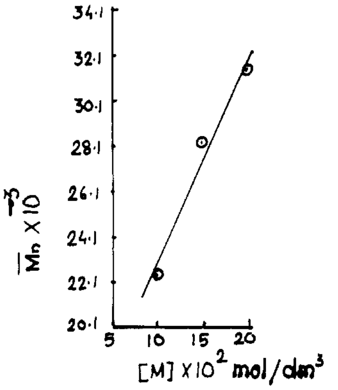

Figure 1. Variation of molecular weight with initial concentration of monomer at fixed [$KMnO_4$] = 4.0 × 10^{-3} mol/dm^3, [L-serine] = 19.2 × 10^{-2} mol/dm^3, and [H^+] = 3.5 × 10^{-2} mol/dm^3 at 35 ± 0.2 °C.

This type of fast decomposition of radical A to B is analogous to the aliphatic series reaction

$$CH_3CH(OH)COO\cdot \rightarrow CH_3\dot{C}H(OH) + CO_2 \quad (5)$$

suggested by Waters.[9] For this reason radical B would be the main initiating species in the present studies.

(b) Initiation

$$B + M\ (\text{acrylamide}) \xrightarrow{k_i} M\cdot \quad (6)$$

(c) Propagation

$$M\cdot + M \xrightarrow{k_p} M_1\cdot \quad (7a)$$

$$M_1\cdot + M \xrightarrow{k_p'} M_2\cdot \quad (7b)$$

$$M_{n-1}\cdot + M \xrightarrow{k_p''} M_n\cdot \quad (7c)$$

(d) Termination

$$M_n\cdot \xrightarrow{k_t} \text{polymer} \quad (8)$$

The unimolecular termination has been proposed on the basis of experimental observation, i.e., first-order correlation between the rate of polymerization and catalyst concentration. Termination by the dissolved metal ions Mn^{3+}/Mn^{4+} may also not be ignored. A similar type of observation was also made by Watanabe et al.[10]

Rate of Polymerization. The initial rate of polymerization (R_p) was found to increase linearly with increasing acrylamide concentration in the studied range ((5.0–20) × 10^{-2} mol/dm^3). A plot of log R_p vs. log [M] was found to be linear with a slope of 0.95, thus indicating that the order of reaction with respect to monomer was unity. At various initial monomer concentrations, the molecular weight of the resulting polymer was determined and a linear relationship between the initial monomer concentration and molecular weight was obtained (Figure 1). This is in good agreement with the results reported by others.[11]

The rate of polymerization also increases with increasing concentrations of L-serine ((9.5–26.6) × 10^{-2} mol/dm^3) and permanganate ((2.4–7.2) × 10^{-3} mol/dm^3). With an increase of the activator and catalyst concentrations, the number of initiating species increases, which in turn increases the initial rate of polymerization and maximum conversion. The order with respect to L-serine has been found to be 1.06 from a double-logarithmic plot (Figure 2, curve a). The first-power correlation between rate and catalyst concentration has also been observed from the double-logarithmic plot (Figure 3, curve a). The first power with respect to catalyst confirms the unimolecular mechanism for the termination process. The first-order rate dependence with respect to activator and catalyst has also been observed in previously studied permanganate–amino acid systems.[4,5] Similar results were also reported by Bajpai[12] and Hussain et al.[13]

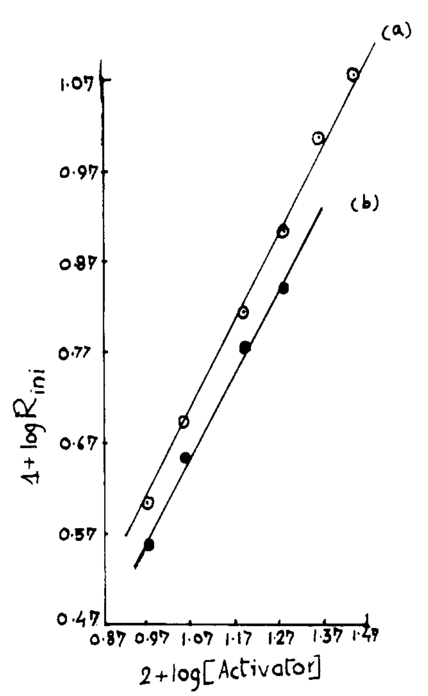

Figure 2. Double-logarithmic plot of the initial rate of polymerization (R_{in} in percent conversion per minute) vs. the initial concentration of activator (L-serine): (a) in aqueous medium; (b) in the presence of 5% (v/v) DMF. Slope = 1.06 in both cases.

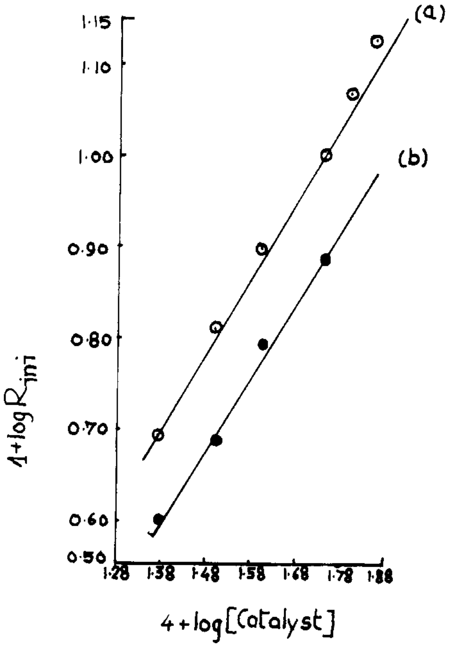

Figure 3. Double-logarithmic plot of the initial rate of polymerization (R_{in} in percent conversion per minute) vs. the initial concentrations of catalyst ($KMnO_4$): (a) in aqueous medium; (b) in the presence of 5% (v/v) DMF. Slope = 0.90 in both cases.

pH Effect. The effect of pH of the reaction medium on the rate of polymerization has been studied by the addition of varying amounts of sulfuric acid in the range (1.5–5.25) × 10^{-2} mol/dm^3, i.e., with decreasing pH from 3.7 to 3.45. The rate of polymerization and maximum

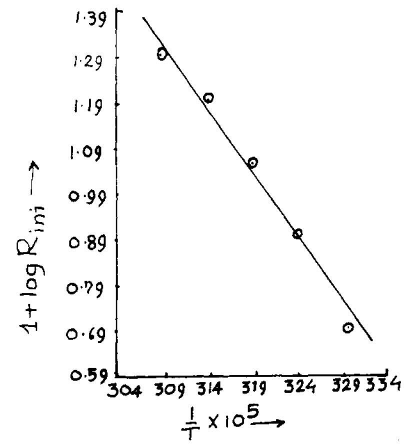

Figure 4. Arrhenius plot. [Monomer] = 10.0 × 10^{-2} mol/dm^3, [KMnO$_4$] = 4.0 × 10^{-3} mol/dm^3, and [L-serine] = 19.2 × 10^{-2} mol/dm^3. Energy of activation E_a = 12.9 kcal/mol (53.92 kJ/mol).

conversion was found to increase within the pH range 3.75–3.50, which may be explained as follows:

(i) With an increase of the concentration of H$^+$ ions, the concentration of protonated L-serine increases (eq 1), which in turn increases the number of initiating species.

(ii) In acid medium, two consecutive redox systems, viz., permanganate–reducing agent and permanganate–acid, operate. By the addition of H$^+$ ions, the latter system generates more initiating species, which accelerates the rate. A further decrease in pH (<3.50) causes depression in the initial rate and maximum conversion, which may probably be due to the reduction of Mn^{4+} ions to Mn^{2+} by excess H$^+$ ions with the liberation of inhibiting oxygen (eq 9). No polymerization occurs at and below pH 3.30. The initial rate and maximum conversion fall when the pH of the reaction medium is raised above 3.70. Beyond pH 3.75 no polymerization occurs, as the acid present is not sufficient to dissolve MnO$_2$ produced by the interaction of permanganate and monomer.

$$MnO_2 + 2H^+ \rightarrow Mn^{2+} + H_2O + O \qquad (9)$$

Temperature Effect. The initial rate of polymerization was found to increase with increasing temperature from 30 to 50 °C, but the maximum conversion decreases above 35 °C. The increase in rate is expected due to the rise in active-center formation with increase in temperature, but the decrease in maximum conversion may be because of newly born side reactions that increase the probability of primary radicals to undergo termination at a relatively faster rate. The overall energy of activation as calculated from the Arrhenius plot (Figure 4) has been found to be 12.9 kcal/mol.

Effect of Water-Miscible Organic Solvents. Addition of 5% (v/v) water-soluble organic solvents like methanol, ethanol, DMF, dioxane, 2-propanol, and 1-butanol in the reaction medium reduce the initial rate as well as maximum conversion (Figure 5) but the kinetic expression remains unaltered. The order of reaction with respect to activator and catalyst in 5% DMF–water medium remains unity (Figure 2, curve b; Figure 3, curve b). The fall in rate and limiting conversion may be explained as follows:

(i) The addition of water-miscible organic solvents decreases the area of shielding of a strong hydration layer in aqueous medium, resulting in the termination of a radical end of a growing chain.

(ii) In the presence of these solvents, some oxidant (KMnO$_4$) is consumed in their oxidation, and thus the catalyst concentration in the reaction medium is reduced, which results in a fall in the rate and limiting conversion.

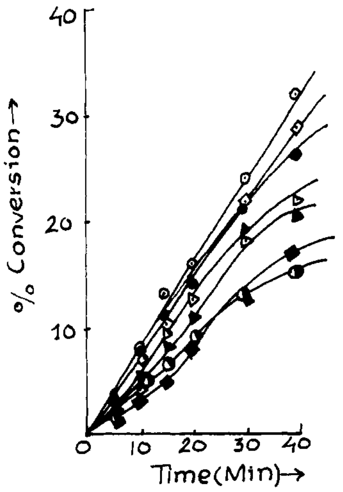

Figure 5. Plot of initial course of polymerization of acrylamide in various media at fixed [monomer] = 10.0 × 10^{-2} mol/dm^3, [KMnO$_4$] = 4.0 × 10^{-3} mol/dm^3, [L-serine] = 19.2 × 10^{-2} mol/dm^3, and [H$^+$] = 3.5 × 10^{-2} mol/dm^3 at 35 ± 0.2 °C: (■) dioxane (5% (v/v)); (◑) 1-butanol (5% (v/v)); (▲) 2-propanol (5% (v/v)); (◭) ethanol (5% (v/v)); (⊡) DMF (5% (v/v)); (●) methanol (5% (v/v)); (⊙) H$_2$O medium.

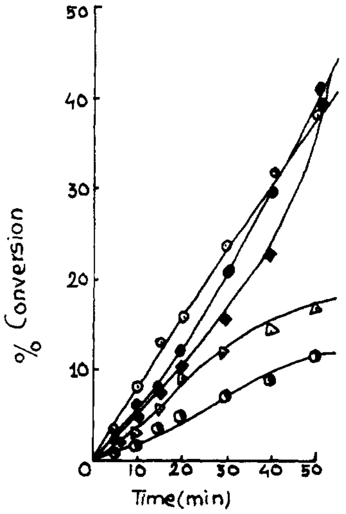

Figure 6. Effect of complexing agents on the plot of initial course of polymerization of acrylamide at fixed [monomer] = 10.0 × 10^{-2} mol/dm^3, [KMnO$_4$] = 4.0 × 10^{-3} mol/dm^3, [L-serine] = 19.2 × 10^{-2} mol/dm^3, and [H$^+$] = 3.5 × 10^{-2} mol/dm^3 at 35 ± 0.2 °C: (◑) [EDTA] = 2 × 10^{-3} mol/dm^3; (◭) [EDTA] = 1 × 10^{-3} mol/dm^3; (⊙) no salt added; (■) [NaF] = 2 × 10^{-2} mol/dm^3; (●) [NaF] = 1 × 10^{-2} mol/dm^3.

(iii) Due to the transfer of macroradical chains to these solvents, a decrease in the rate may also be observed. The newly formed sluggish radical may not be capable of initiating the polymerization again.

When these solvents are added in equal quantity (5% (v/v)), the order of depression of the rate of polymerization and the increase in induction period is found as methanol < DMF < ethanol < 2-propanol < 1-butanol < dioxane.

Effect of Complexing Agents. The effect of complexing agents like NaF and EDTA on the course of polymerization has been studied (Figure 6). Both NaF and EDTA depress the rate of polymerization. The maximum conversion has been found to increase in the case of NaF. The depression caused by NaF may be due to a complex formation, believed to be MnF$_4^-$, between Mn^{3+} and fluoride ions. Thus Mn^{3+} ions are prevented from participating in the radical generation process, resulting in

Table I

surfactant	chain length	concn × 10^3, mol/dm^3	CMC × 10^3, mol/dm^3	effect on R_p
cetyltrimethylammonium bromide, CTAB (cationic)	C_{16}	0.1–1.64	0.82	increased below and above CMC
sodium oleate (anionic)	C_{18}	0.03–0.15	0.05	decreased below and above CMC

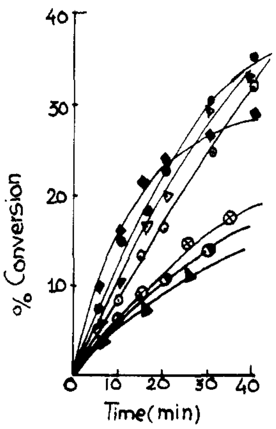

Figure 7. Effect of surfactants on the plot of initial course of polymerization of acrylamide at fixed [monomer] = 10.0×10^{-2} mol/dm^3, [$KMnO_4$] = 4.0×10^{-3} mol/dm^3, [L-serine] = 19.2×10^{-2} mol/dm^3, and [H^+] = 3.5×10^{-2} mol/dm^3 at 35 ± 0.2 °C: (▲) [sodium oleate] = 1.5×10^{-4} mol/dm^3; (◑) [sodium oleate] = 0.5×10^{-4} mol/dm^3; (⊕) [sodium oleate] = 0.3×10^{-4} mol/dm^3; (⊙) no surfactant added; (△) [CTAB] = 0.1×10^{-3} mol/dm^3; (●) [CTAB] = 0.82×10^{-3} mol/dm^3; (■) [CTAB] = 1.64×10^{-3} mol/dm^3.

the depression of polymerization rate. The increase in the maximum conversion may be due to the disintegration of the complex formed at a later stage liberating Mn^{3+} ions. Similar results were also found by Misra et al.[14,15] The depression in rate and maximum conversion caused by EDTA may be due to the formation of a relatively stable chelate with Mn^{4+} ions. The formation of nonradical ions in the system also brings a reduction in rate. Shukla et al.[16] also reported similar results.

Effect of Surfactants. In the recent past miceller catalysts have played an important role in kinetic investigations of the mechanism of certain polymerization reactions. The influence of surfactants on the polymerization rate has been summarized in Figure 7 and Table I.

Addition of cationic surfactant CTAB to the reaction medium enhanced the rate and maximum conversion. This increase may be explained as follows:

(i) The polar end of the chain of the cationic surfactant and the charged growing polyradicals obtained by the incorporation of radicals A and B are not subjected to Coulombic attractions. Thus the premature termination of growing chain is not possible.

(ii) As the reaction is acid-catalyzed, H^+ ions are helped by the positively charged hydrocarbon chain of the detergent in combining with L-serine, which ultimately gives free radicals after oxidation. Similar results were obtained by Shukla et al.[17]

The addition of anionic surfactants such as sodium oleate decreases the rate of polymerization and maximum conversion. The retarding effect of the anions may be explained by specific ion-pair binding of the cation Mn^{3+} with anions, which lowers the rate of primary radical generation. Also, H^+ ion catalyzed formation of protonated L-serine is hindered due to an appreciable interaction between the anions and the H^+ ion, which finally results in the slow formation of free radicals. The free oleic acid, as produced by interaction of the anions and the H^+ ions will also interfere with normal polymerization reactions and therefore will cause depression in the initial rate and maximum conversion. Similar results were reported by Shukla et al.[18]

Conclusion

The rate of polymerization varies linearly with the concentration of oxidant, reductant, and monomer in the studies range. The kinetic expression remains unchanged when polymerization is carried out in water–DMF mixtures. The initial rate and limiting conversion is effected by the addition of complexing agents, organic solvents, detergents, etc. The number-average molecular weight increases with increasing monomer concentration.

Acknowledgment. We are thankful to CSIR, India, for financial assistance to A.K.B.

Registry No. Acrylamide, 79-06-1; L-serine, 56-45-1; potassium permanganate, 7722-64-7; polyacrylamide, 9003-05-8; cetyltrimethylammonium bromide, 57-09-0.

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