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Kinetics of Polymerization of Methyl Methacrylate Initiated by the Redox System Mn^{3+}/Crotonic Acid

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ABSTRACT

The kinetics of polymerization of methyl methacrylate initiated by the redox system Mn^{3+}/crotonic acid was studied in aqueous sulfuric acid in the temperature range of 35-50°C, and the rates of polymerization (R_p), Mn^{3+} disappearance, etc. were measured. The effect of certain water miscible organic solvents, some neutral electrolytes, and solid substances on the rates of polymerization has been investigated. A mechanism involving the formation of a complex between Mn^{3+} and crotonic acid whose decomposition yields the initiating free radical with the polymerization being terminated by the metal ion has been suggested.

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INTRODUCTION

Redox polymerization initiated by heavy metal ions such as Co^{3+}, Ce^{4+}, V^{5+}, Cr^{6+}, and Mn^{3+} has attracted attention in recent years [1-21] since it throws light regarding the mechanistic details of individual steps. Water's school [22] has investigated the oxidation kinetics of a multitude of organic substrates involving trivalent manganese. Mn^{3+}, either in the form of sulfate or pyrophosphate, reacts with simple organic molecules to form a complex which decomposes in a unimolecular step to produce a free radical which initiates polymerization. Singh et al. [23] and Namasivayam et al. [24] have reported that manganic sulfate in an excess of sulfuric acid may form an effective redox system for grafting of polymethyl methacrylate onto cellulose and polyvinyl alcohol. Recently Nayudamma and colleagues [25] have reported Mn^{3+}-initiated graft copolymerization of vinyl monomers onto collagen. We have reported the polymerization of acrylonitrile [6-15], methyl acrylate, methyl methacrylate [15-21], and acrylamide [26] using a number of metal ions such as V^{5+}, Cr^{6+}, Mn^{3+}, etc. and a multitude of organic substrates. In this laboratory there is a program of grafting different vinyl monomers onto nylon 6, wool, silk, and collagen by using Mn^{3+} ion with suitably effective activators. As a part of the research program, we wish to present in this communication the results of aqueous polymerization of methyl methacrylate (MMA) initiated by the Mn^{3+}/crotonic acid redox system. From the experimental results, a suitable reaction scheme has been suggested and various kinetic parameters are evaluated.

EXPERIMENTAL

Methyl methacrylate was purified according to our previous method [16]. The crotonic acid used was of BDH AnalaR grade. Mn(II) sulfate was an EM-GR product. All other reagents, such as ferrous ammonium sulfate and o-phenanthroline, were commercial products, either BDH(AR) or E. Merck (GR). Manganese(III) stock solutions were prepared by electrolytic oxidation of an appropriate Mn^{2+} salt solution (0.4-0.6 $\underline{M}$) in 3.5-6 $\underline{M}$ sulfuric acid at the platinum anode [27, 28] and was analyzed for Mn^{3+} content by EDTA titration [29]. Water distilled thrice over alkaline permanganate and deionized by passing it through a column of Biodeminrolit resin (Permutit Co., U.K.) was used to prepare all solutions. The nitrogen (Indian Oxygen Co., Calcutta) used was purified by passing it through the columns of Fieser's solution, a column of saturated lead acetate solution, and finally through a wash bottle containing deionized water.

The reaction was carried out in a Pyrex tube fitted with B29 sockets and closed by B24 cones equipped with glass inlet and outlet tubes. The polymerization reactions were heterogeneous with polymer

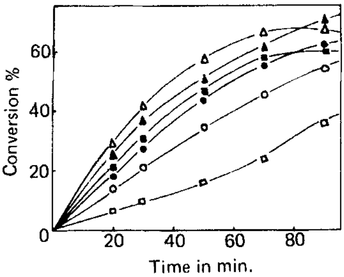

FIG. 1. Variation of percentage conversion with time, effect of activator concentration. For [Mn^{3+}] = 7 × 10^{-3} M, [H^+] = 1 M, μ = 2.6 M, [MMA] = 0.09388 M, and 40°C, the [CA] values are (●) 1.5 × 10^{-2} M, (▲) 2 × 10^{-2} M, (■) 2.5 × 10^{-2} M, and (○) 3 × 10^{-2} M. For [Mn^{3+}] = 7 × 10^{-3} M, [H^+] = 1 M, μ = 2.6 M, [MMA] = 0.09388 M, and [CA] = 2 × 10^{-2} M, the temperatures are (□) 35°C and (△) 45°C.

precipitating continuously. Rates of polymerization (initial rates) were obtained gravimetrically, while the rates of oxidant consumption were obtained by cerimetry on reaction mixtures arrested by addition of excess standard ferrous ammonium sulfate solution.

RESULTS AND DISCUSSION

Methyl methacrylate was polymerized in aqueous sulfuric acid solution at 35-50°C in the presence of the redox system Mn^{3+}/crotonic acid. Typical sets of time conversion plots at 40°C and at various crotonic acid concentrations (0.015-0.03 M) and the effect of temperature are shown in Fig. 1.

Rate of Manganic Ion Disappearance

The rates of manganic ion disappearance ($-d[Mn^{3+}]/dt$) were first order in [Mn^{3+}] and independent of monomer [MMA] concentration. Plots of $(-d[Mn^{3+}]/dt)^{-1}$ vs $[CA]^{-1}$ (where CA represents crotonic acid) were linear with their intercepts on the rate axis, which shows Lineweaver-Burk kinetics [30] for complex formation (Fig. 2). Similar complex formation has been illustrated by Waters and coworkers in the case of malonic acid oxidation by Mn^{3+}.

Rate of Polymerization

The rate of polymerization was found to increase linearly with

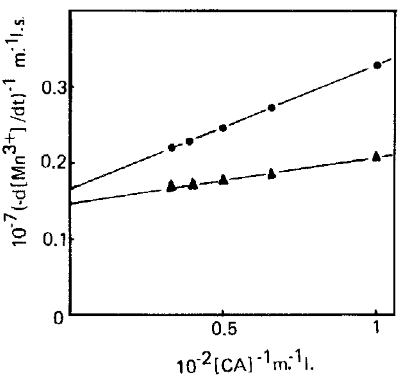

FIG. 2. Variation of R_p with substrate at different temperatures with $[Mn^{3+}] = 7 \times 10^{-3}$ M, $[H^+] = 1$ M, and $\mu = 2.6$ M: (●) 35°C and (▲) 40°C.

increasing monomer concentration (0.04644-0.2347 M). The plots of R_p vs [MMA] were linear, passing through the origin (Fig. 3) and showing that the order was unity with respect to [MMA]. The rate of polymerization was found to increase with an increase in the concentration of crotonic acid (Fig. 4), but deviation from normal behavior has been observed at higher concentrations. This might be due to the increase in viscosity of the medium which hinders the termination of the growing polymer radical.

Effect of Water-Miscible Organic Solvents

Additions of 5% (v/v) water miscible organic solvents such as ethanol, acetone, acetic acid, and DMF are found to depress considerably the rate of polymerization as well as the maximum conversion (Fig. 5). Most probably these solvents decrease the area of shielding of the strong hydration layer in aqueous medium, resulting in the termination of the radical end of the growing chain. These solvents increase the regulated rate of production of primary radicals which under the existing experimental conditions renders the termination rate relatively fast as compared to the rate of growth of the polymer chain as pointed out by Kern et al. [31]. Further, the interchain hydrogen bonding interlocking the polymer chain is not rigid (strong), whereby the tendency of mutual termination of the polymer chain increases. Similar observations have been noted by Mishra et al. in the case of aqueous polymerization of acrylamide. We have also noticed the same observation in the case of the polymerization of acrylamide initiated by quinquevalent vanadium/cyclohexanone and

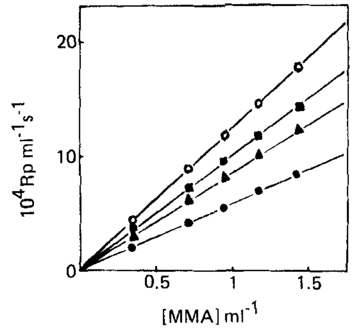

FIG. 3. Variation of R_p with monomer concentration with $[Mn^{3+}] = 7 \times 10^{-3}$ M, $[H^+] = 1$ M, $[CA] = 2 \times 10^{-2}$ M, and $\mu = 2.6$ M: (●) 35°C, (▲) 40°C, (■) 45°C, and (○) 50°C.

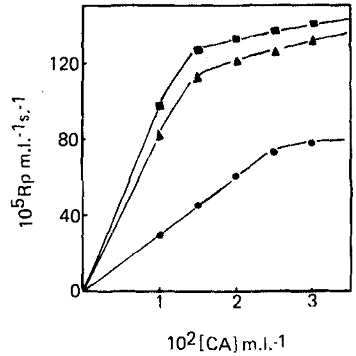

FIG. 4. Variation of R_p with substrate concentration with $[Mn^{3+}] = 7 \times 10^{-3}$ M, $[H^+] = 1$ M, $\mu = 2.6$ M, and $[MMA] = 0.09388$ M: (●) 35°C, (▲) 40°C, and (■) 45°C.

the polymerization of acrylonitrile initiated by Mn^{3+}/citric acid redox system.

Effect of Added Electrolytes

Addition of certain neutral electrolytes such as KCl, Na_2SO_4, $CuSO_4$, and $ZnSO_4$ (0.02 M) to the reaction mixture depresses the rate of polymerization as well as the maximum conversion. This is probably due to the fact that the ability of the catalytic activity of Mn^{3+} to

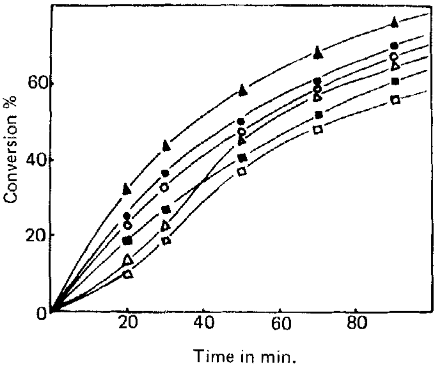

FIG. 5. Variation of percentage conversion with time in the presence of water-miscible organic solvents and solid substance with $[Mn^{3+}] = 7 \times 10^{-3}$ $\underline{M}$, $[CA] = 2 \times 10^{-2}$ $\underline{M}$, $[MMA] = 0.09388$ $\underline{M}$, $[H^+] = 1$ $\underline{M}$, $\mu = 2.6$ $\underline{M}$, and temperature = 40°C: (●) control, (■) [ethanol] = 5% (v/v), (○) [acetone] = 5% (v/v), (△) [acetic acid] = 5% (v/v), (□) [DMF] = 5% (v/v), and (▲) silica = 1 g.

produce the free radical is greatly reduced due to ion-pair coupling of the added electrolytes.

Effect of Complexing Agents

On addition of 0.02 $\underline{M}$ complexing agents like NaF, succinic acid, pyridine, and lutidine, the initial rate and the maximum conversion were depressed considerably (Fig. 6), and with aniline as the complexing agent the reaction was completely inhibited. The most probable explanations for this type of behavior are that the pH of the medium changes due to consumption of the H^+ ion by the amines and that the activity of the Mn^{3+} ion is greatly reduced due to complex formation with the amines behaving as ligands.

Effect of Temperature

With an increase of temperature the initial rate as well as the maximum conversion increases appreciably (Fig. 1). The dependence of the rate of polymerization with an increase in temperature can be ascribed to the greater activation energy.

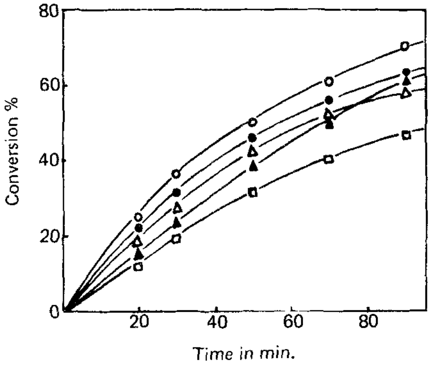

FIG. 6. Variation of percentage conversion with time in the presence of some complexing agents with [Mn^{3+}] = 7 × 10^{-3} M, [CA] = 2 × 10^{-2} M, [MMA] = 0.09388 M, [H^+] = 1 M, μ = 2.6 M, and temperature = 40°C: (○) control, (△) [NaF] = 0.02 M, (□) [succinic acid] = 0.02 M, (●) [pyridine] = 0.02 M, and (▲) [lutidine] = 0.02 M.

Effect of Solid Substances

The initial rate and maximum conversion were increased when the reaction was carried out in the presence of silica (Fig. 5). A similar observation was made by Maustafa et al. [32] in the polymerization of MMA in the presence of graphite. The behavior of silica in the polymerization of MMA is complex, and the catalytic effect may be attributed to the fact that it decreases the apparent activation energy for the polymerization of MMA and increases the active centers present at certain spots.

Reaction Mechanism and Rate Law

Heterogeneity is a characteristic feature of the polymerization of methyl methacrylate in aqueous media. The reaction mixture, although homogeneous before the initiation of polymerization, becomes heterogeneous as soon as the polymerization starts due to the insolubility of the polymer in the aqueous phase.

From the proportionalities obtained between the measurable parameters and the variables, a reaction scheme has been suggested involving initiation by the organic free radical produced by the interaction of Mn^{3+} with crotonic acid and termination by Mn^{3+} ion. The termination by metal ion has been suggested in our previous communications:

$$\mathrm{Mn_{eq}}^{3+} + CA \underset{}{\overset{K}{\rightleftharpoons}} \text{complex} \tag{1}$$

$$\text{Complex} \xrightarrow{k_r} \mathrm{R}^{\bullet} + \mathrm{Mn}^{2+} + \mathrm{H}^{+} \tag{2}$$

$$\mathrm{R}^{\bullet} + \mathrm{Mn}^{3+} \xrightarrow{k_0} \text{products} \tag{3}$$

$$\mathrm{R}^{\bullet} + \mathrm{M} \xrightarrow{k_i} \mathrm{RM_1}^{\bullet} \tag{4}$$

$$\mathrm{RM_1}^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{RM_2}^{\bullet} \tag{5}$$

$$\mathrm{RM_{n-1}}^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{RM_n}^{\bullet} \tag{6}$$

$$\mathrm{RM_n}^{\bullet} + \mathrm{Mn_{eq}}^{3+} \xrightarrow{k_t} \text{polymer} + \mathrm{Mn}^{2+} + \mathrm{H}^{+} \tag{7}$$

By making the usual steady-state approximation, we can arrive at the following expressions:

$$d[\mathrm{R}^{\bullet}]/dt = k_r[\text{complex}] - k_i[\mathrm{R}^{\bullet}][\mathrm{M}] - k_0[\mathrm{R}^{\bullet}][\mathrm{Mn}^{3+}]_{eq} = 0 \tag{8}$$

$$[\mathrm{R}^{\bullet}] = \frac{k_r[\text{complex}]}{k_i[\mathrm{M}] + k_0[\mathrm{Mn}^{3+}]_{eq}} \tag{9}$$

$$= \frac{k_r K[\mathrm{Mn}^{3+}]_{eq}[\mathrm{CA}]}{(k_i[\mathrm{M}] + k_0[\mathrm{Mn}^{3+}]_{eq})} \tag{10}$$

The steady-state expression for $\mathrm{R_{Mn}}^{\bullet}$ will be

$$[\mathrm{R_{Mn}}^{\bullet}] = \frac{k_i k_r K[\mathrm{CA}][\mathrm{M}]}{(k_i[\mathrm{M}] + k_0[\mathrm{Mn}^{3+}]_{eq})k_t} \tag{11}$$

If $k_p[\mathrm{R_{Mn}}^{\bullet}][\mathrm{M}] \gg k_i[\mathrm{R}^{\bullet}][\mathrm{M}]$, rates of polymerization will be given by

$$-d[M]/dt = \frac{k_p k_i k_r K[M]^2[CA]}{k_t(k_i[M] + k_0[Mn^{3+}]_{eq})} \qquad (12)$$

The above equation requires that k_p be second order with respect to monomer, which decreases with increasing $[Mn^{3+}]$.

If, on the other hand, reaction step (3) were unimportant, with primary radical being effectively scavenged by the monomer, $(k_i[M] \gg k_0[Mn^{3+}]_{eq})$, we could get

$$[R_{Mn}^\bullet] = k_r K[CA]/k_t \qquad (13)$$

Hence,

$$R_p = k_p k_r K[CA][M]/k_t \qquad (14)$$

Further, the rates of oxidant consumption would be given by

$$-d[Mn^{3+}]/dt = k_r K[Mn^{3+}]_{eq}[CA] + k_t[R_{Mn}^\bullet][Mn^{3+}]_{eq} \qquad (15)$$

Substituting the above values of $R_{Mn}^\bullet$ into Eq. (13), we get

$$-d[Mn^{3+}]/dt = 2k_r K[Mn^{3+}]_{eq}[CA] \qquad (16)$$

Since

$$[Mn^{3+}]_{total} = [Mn^{3+}]_{eq}(1 + K[CA]) - d[Mn^{3+}]/dt$$

$$= 2k_r K[Mn^{3+}]_{total}[CA]/(1 + K[CA]) \qquad (17)$$

Equation (17) can be rearranged as

$$(-d[Mn^{3+}]/dt)^{-1} = \frac{1}{2k_r K[Mn^{3+}]_{total}[CA]} + \frac{1}{2k_r[Mn^{3+}]_{total}} \qquad (18)$$

According to Eq. (18), the plots of $(-d[Mn^{3+}]/dt)^{-1}$ vs $[CA]^{-1}$ (Fig. 2) are linear with the intercept on the ordinate.

From the intercepts and the ratio of the intercept/slope of these plots, the rate of unimolecular decomposition of the complex (k_r) and the formation constant (K) were computed. (Values of $k_r = 5.7 \times 10^{-3}$ and 10.8×10^{-3} s^{-1} at 40 and 45°C and values of $k_r = 4.9$ and 10.3 l/mol at 40 and 45°C, respectively.)

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