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Kinetics of Polymerization of Methyl Methacrylate Initiated by the V^{5+}/Thioacetamide Redox System

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ABSTRACT

Kinetics of the polymerization of methyl methacrylate has been investigated in aqueous sulfuric acid in the temperature range of 35-50°C in the presence of the redox system V^{5+}/thioacetamide. The rate of polymerization and the rate of V^{5+} ion disappearance have been measured. The effect of various additives such as water-miscible organic solvents, neutral electrolytes, complexing agents, and solvent composition on the rate have been thoroughly studied. A mechanism involving the initial complex formation between the thiol form of the thioacetamide and V^{5+}, whose decomposition yields the initiating free radical, with the polymer chain terminated by metal ion has been suggested.

INTRODUCTION

The aqueous vinyl polymerization initiated by metal ions in their higher valence states (Co^{3+}, Ce^{4+}, Cr^{6+}, Mn^{3+}, V^{5+}) have provided valuable information regarding the mechanistic details of individual steps [1-4]. Palit et al. [5] have reported the use of redox systems for the

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initiation of polymerization. Littler and Waters [6] have reported that V^{5+} in the presence of reducing agents such as hydroxy acids, ketones, and glycols initiated vinyl polymerization and have shown that most reactions proceed via a free radical mechanism wherein V^{5+} undergoes only a one-electron reduction. Pentavalent vanadium was employed [7-9] as initiator of graft copolymerization in systems of polymer backbones containing groups such as $-CHO$, $=CO$, or $-NH_2$ which are capable of being oxidized to free radicals on the backbone and a suitable monomer which is grafted. Nayak et al. have reported the polymerization of acrylonitrile [10, 11] methyl acrylate, and methyl methacrylate [12] using V^{5+}/reductant redox systems and the use of thioacetamide [13-15] as the reductant for the polymerization of acrylonitrile. A survey of the literature reveals that not much is known of the kinetics of the vinyl polymerization initiated by the V^{5+}/reducing agent system. The results of kinetics of polymerization of methyl methacrylate initiated by the V^{5+}/thioacetamide redox system in aqueous sulfuric acid in the temperature range 35-50°C are reported in this article. From the experimental observations, a suitable reaction scheme is suggested.

EXPERIMENTAL

Methyl methacrylate (Rohm and Hass, U.S.A.) monomer was purified by standard methods. Ammonium metavanadate (A.R), thioacetamide (A.R), Sodium sulfite (Riedel), ferrous ammonium sulfate (A.R), and sulfuric acid (18 M; A.R., B.D.H.) were used. Water, distilled twice over alkaline permanganate and de-ionized by passing through a column of Biodermінrolit resin (Permutit Co., United Kingdom) was used to prepare all solutions. The nitrogen (Indian Oxygen Co., Calcutta) used to de-aerate the experimental systems was freed from oxygen by passage through five columns of Fieser's solution, a column of saturated lead acetate solution, and finally through a wash bottle containing distilled water. A stock solution of V^{5+} was prepared as described by Nayak et al. [10]. The concentration of V^{5+} in the experimental systems was determined by vanadometry [17]. An aliquot (2 cm^3) of V^{5+} stock solution was run into a known excess of standard ferrous ammonium sulfate solution. The excess of Fe^{2+} was titrated with standard V^{5+} (0.01-0.02 N) using Knop's indicator followed by addition of 5 cm^3 of 80% orthophosphoric acid to a violet end point.

The reactions were heterogeneous and there was no evidence for any induction period in completely de-aerated systems. Rates of oxidant consumption were obtained by titrimetry, whereas those of polymerization were obtained gravimetrically.

RESULTS AND DISCUSSION

Methyl methacrylate was polymerized in aqueous sulfuric acid solution at 35-50°C in the presence of the redox system V^{5+}/ thioacetamide. A typical set of time conversion curves at 40°C at various thioacetamide concentrations (0.5×10^{-2} to 2.5×10^{-2} M) is shown in Fig. 1.

Rate of Polymerization: R_p

The rate of polymerization ($R_p = -d[M]/dt$) increased with an increase of monomer concentration. Plots of R_p versus [MMA] [2] were linear, passing through the origin (Fig. 2), and showing that the order with respect to [MMA] was 2.

R_p was found to decrease with an increase of $[V^{5+}]$, and the plots of $1/R_p$ vs $[V^{5+}]$ were linear with intercepts (Fig. 3). R_p was found to increase with an increase of [TA] (Fig. 4) (where TA represents thioacetamide).

Linear plots of log R_p versus log [TA] with "unit slopes" as well as zero intercepts indicated that the order with respect to [TA] was unity. The increase of rate with an increase of $[HSO_4^-]$ may be understood in terms of

$$VO_2^+ + HSO_4^- \rightleftharpoons VO_2SO_4^- + H^+ \tag{1}$$

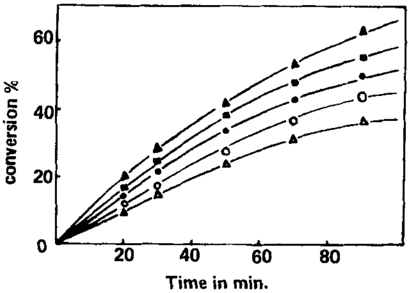


FIG. 1. Variation ot percent conversion at different activator concentrations. $[V^{5+}] = 1.5 \times 10^{-2}$ M, $[H^+] = 0.9$ M, [MMA] = 0.09388 M, $\mu = 2.3$ M, temperature = 40°C. [TA]: (●) 0.5×10^{-2} M, (▲) 1×10^{-2} M, (■) 1.5×10^{-2} M, (○) 2×10^{-2} M, (△) 2.5×10^{-2} M.

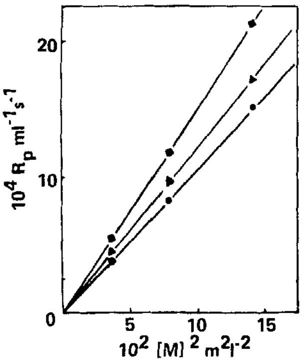


FIG. 2. Variation of R_p with monomer concentration at different temperatures. $[V^{5+}] = 2 \times 10^{-2}$ M, $[H^+] = 0.9$ M, [TA] $= 1 \times 10^{-2}$ M, $\mu = 2.3$ M. Temperatures: (●) 35°C, (▲) 40°C, (■) 45°C.

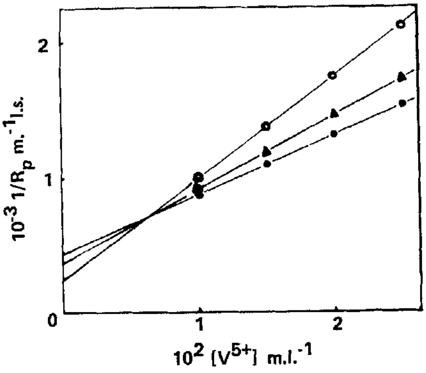


FIG. 3. Variation of R_p with catalyst concentration at different temperatures. $[H^+] = 0.9$ M, [TA] $= 1 \times 10^{-2}$ M, $\mu = 2.3$ M, [MMA] = 0.09388 M. Temperatures: (○) 40°C, (▲) 45°C, (●) 50°C.

This also indicates that the bisulfate complexes of V^{5+} are more effective initiators or less effective terminators. R_p was found to be independent of [H_2SO_4] (2-4 mol/L). Similar results were obtained by Santappa et al. [17] and Nayak et al. [10] in the case of acrylonitrile polymerization. R_p increased with the ionic strength (μ), i.e., when sodium perchlorate and zinc sulfate were used to adjust the ionic

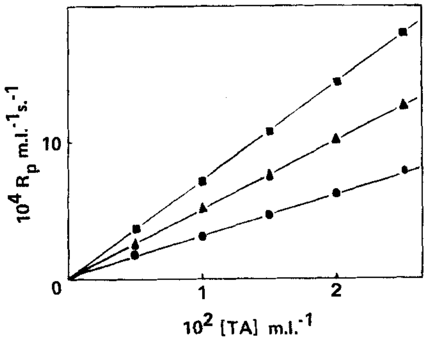


FIG. 4. Variation of R_p with substrate concentration at different temperatures. $[V^{5+}] = 2 \times 10^{-2}$ M, $[H^+] = 0.9$ M, [MMA] = 0.09388 M, $\mu = 2.3$ M. Temperatures: (●) 35°C, (▲) 40°C, (■) 45°C.

strength. This increasing rate may be understood in terms of a catalysis of the salts in the propagation step.

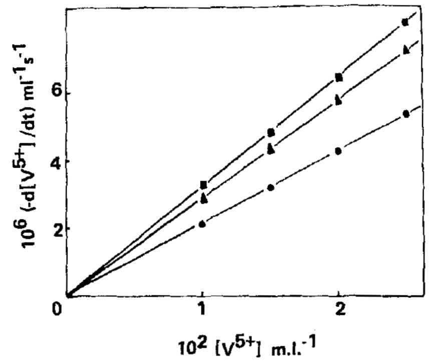
Rate of V^{5+} Disappearance ($-R_V$)

The rate of V^{5+} disappearance ($-R_V$) was found to be independent of the monomer concentration. An increase in $[V^{5+}]$ (1×10^{-2} to 2.5×10^{-2} M) increases the rate. Hence the rate of V^{5+} ion disappearance ($-d[V^{5+}]/dt$) was first order in $[V^{5+}]$. Plots of $-R_V$ versus $[V^{5+}]$ are linear (Fig. 5a).

An increase of [TA] increases the rate, and the plot of $-R_V$ versus [TA] is linear, passing through the origin (Fig. 5b).

Effect of Water Miscible Organic Solvents

Addition of 10% (v/v) water-miscible organic solvents such as acetic acid, acetone, ethanol and chloroform to the reaction mixture depresses the initial rate as well as maximum conversion. The retarding effect of these solvents may be due to the following reasons: (1) solvent molecules might decrease the area of shielding of a strong hydration layer in aqueous medium, resulting in the termination of the radical end of the growing chain; (2) the decrease in efficiency of the catalyst (V^{5+} ion) as compared to the control process due to the secondary oxidation of the additives; (3) these solvents might 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 polymer chain. This is in agreement with the view of Kern et al. [18]; and (4) the hydrogen



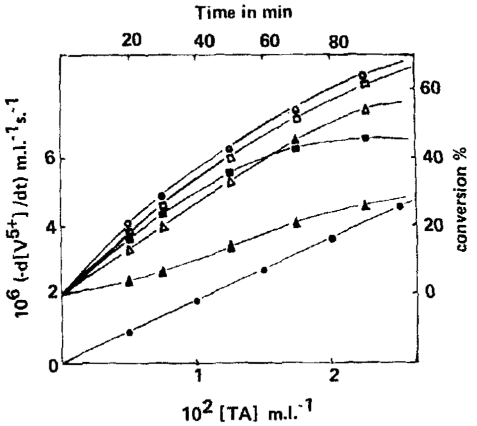


FIG. 5a. Variation of d[V^{5+}]/dt with [V^{5+}] at different temperatures. [H^+] = 0.9 M, [TA] = 1×10^{-2} M, μ = 2.3 M, [MMA] = 0.09388 M. Temperatures: (●) 40°C, (▲) 45°C, (■) 50°C.

FIG. 5b. Variation of percent conversion with time; effect of some neutral electrolytes. [V^{5+}] = 2×10^{-2} M, [H^+] = 0.9 M, [TA] = 1×10^{-2} M, μ = 2.3 M, [MMA] = 0.09388 M, temperature = 40°C: (○) Control, (△) [KCl] = 0.02 M, (□) [Na_2SO_4] = 0.02 M, (▲) [$CuSO_4$] = 0.02 M, (■) [$ZnSO_4$] = 0.02 M. Variation of - d[V^{5+}]/dt with [TA] at 45°C (●): [V^{5+}] = 2×10^{-2} M, [H^+] = 0.9 M, [MMA] = 0.09388 M, μ = 2.3 M.

bonding interlocking with the polymer chain is not rigid (strong) as a result of which the tendency of mutual termination of the polymer chain increases. Nayak et al. [19, 20] have noticed similar behavior in the case of aqueous polymerization of acrylamide initiated by V^{5+}/cyclohexanone and acrylonitrile initiated by Mn^{3+}/citric acid redox

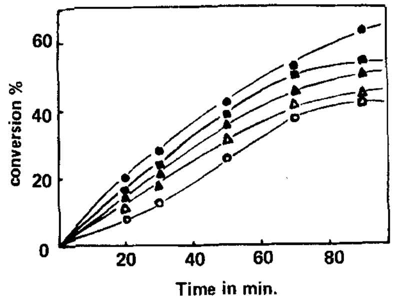


FIG. 6. Variation of percent conversion with time at different acetone concentrations. $[V^{5+}] = 2 \times 10^{-2}$ M, $[H^+] = 0.9$ M, [TA] = 1×10^{-2} M, $\mu = 2.3$ M, [MMA] = 0.09388 M, temperature = 40° C. (●) Control. Acetone concentration: (■) 10% (v/v), (▲) 20% (v/v), (△) 30% (v/v), (○) 40% (v/v).

systems. With the increase of solvent composition, the initial rate as well as the maximum conversion still decreases appreciably (Fig. 6).

Effect of Added Electrolytes

Addition of certain neutral electrolytes such as KCl, Na_2SO_4, and $ZnSO_4$ of 0.02 M concentration to the reaction mixture depresses the rate of polymerization as well as the maximum conversion (Fig. 5b). This is probably caused because the ability of catalytic activity of V^{5+} to produce the free radical is greatly reduced due to ion-pair coupling.

Reaction Mechanism and Rate Law

The polymerization of methyl methacrylate initiated by V^{5+} ion in the presence of thioacetamide alone shows characteristic features of heterogeneous polymerization. The reaction system, though homogeneous before 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, the following reaction scheme is suggested, involving initiation by the organic free radical produced by the interaction of V^{5+} with thioacetamide (TA) and termination by V^{5+} ion. The termination by metal ions is now well recognized [21-23].

Primary Radical Production

$$\mathrm{TA} + \mathrm{VO_2}^{+} \underset{\text{fast}}{\overset{K'}{\rightleftharpoons}} \text{complex I} \xrightarrow[\text{slow}]{k_1} \mathrm{R}^{\bullet} + \mathrm{V}^{4+}$$

$$\mathrm{TA} + \mathrm{V(OH)_3}^{2+} \underset{\text{fast}}{\overset{K''}{\rightleftharpoons}} \text{complex II} \xrightarrow[\text{slow}]{k_2} \mathrm{R}^{\bullet} + \mathrm{V}^{4+} + \mathrm{H_3O}^{+}$$

$$\mathrm{TA} + \mathrm{VO.OH}^{2+} \underset{\text{fast}}{\overset{K'''}{\rightleftharpoons}} \text{complex III} \xrightarrow[\text{slow}]{k_3} \mathrm{R}^{\bullet} + \mathrm{V}^{4+}$$

$$\mathrm{TA} + \mathrm{V(OH)_3HSO_4}^{+} \underset{\text{fast}}{\overset{K^{iv}}{\rightleftharpoons}} \text{complex IV} \xrightarrow[\text{slow}]{k_4} \mathrm{R}^{\bullet} + \mathrm{V}^{4+}$$

$$+ \mathrm{H_2SO_4} + \mathrm{H_2O}$$

where

$$\mathrm{VO_2}^{+} + \mathrm{H_3O}^{+} \overset{K_1}{\rightleftharpoons} \mathrm{V(OH)_3}^{2+}$$

$$\mathrm{V(OH)_3}^{2+} + \mathrm{HSO_4}^{-} \overset{K_2}{\rightleftharpoons} \mathrm{V(OH)_3HSO_4}^{+}$$

$$\mathrm{VO_2}^{+} + \mathrm{H}^{+} \overset{K_3}{\rightleftharpoons} \mathrm{VO.OH}^{2+}$$

In the presence of a monomer (M), the free radical $\mathrm{R}^{\bullet}$ starts the chain reaction as shown below:

Initiation

$$\mathrm{R}^{\bullet} + \mathrm{M} \xrightarrow{k_i} \mathrm{RM}^{\bullet}$$

Propagation

$$\mathrm{RM}^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{RM_2}^{\bullet}$$

$$\mathrm{RM}^{\bullet}_{n-1} + \mathrm{M} \xrightarrow{k_p} \mathrm{RM}_n^{\bullet}$$

Linear Termination by V^{5+}

$$RM_n^{\bullet} + VO_2^{+} \xrightarrow{k_{t1}} \text{Polymer} + V^{4+}$$

$$RM_n^{\bullet} + V(OH)_3^{2+} \xrightarrow{k_{t2}} \text{Polymer} + V^{4+}$$

$$RM_n^{\bullet} + VO.OH^{2+} \xrightarrow{k_{t3}} \text{Polymer} + V^{4+}$$

Reaction of Primary Radical With V^{5+}

$$\left.\begin{array}{l} R^{\bullet} + VO_2^{+} \xrightarrow{k_{01}} \\ R^{\bullet} + V(OH)_3^{2+} \xrightarrow{k_{02}} \\ R^{\bullet} + VO.OH^{2+} \xrightarrow{k_{03}} \end{array}\right\} \quad \text{products} + V^{4+}$$

where M represents the monomer (methyl methacrylate), $RM^{\bullet}$ is the radical formed by the reaction of primary radicals with the monomer, and $RM_n^{\bullet}$ represents the growing polymer radical.

Taking into account the above reaction scheme and applying the steady-state principle to both $[R^{\bullet}]$ and $[RM^{\bullet}]$ separately, the following possible expressions for R_p, -Rv, and the chain length n were derived:

$$R_p = (k_p/k_t)k'[TA][M]^2/\left\{[M] + (k_0/k_i[V^{5+}]\right\} \tag{2}$$

$$-R_v = 2k'[TA][VO_2^{+}] \tag{3}$$

where

$$k' = k_1K' + k_3K_3K'''[H^+]$$

$$k' = k_1K' + k_2K_1K''[H_3O^+]$$

or

$$k' = k_1K' + K_1K^{iv}K_2k_4[H^+][HSO_4^-]$$

$$k_t = k_{t1} = k_{t2} = k_{t3}$$

$$k_0 = k_{01} = k_{02} = k_{03}$$

$$n = (k_p/k_t)[M]/[V^{5+}]$$

The dependence of R_p on $[M^2]$ and on [TA], the dependence of $1/R_p$ on $[V^{5+}]$ and 1/[TA], of $-R_v$ on [TA], on $[V^{5+}]$, and not on [M]; all of them are observed and favor the above scheme.

The other modes of termination–mutual termination and primary radical termination–were discounted since they lead to kinetic expressions which were not applicable to the data. Taking the reciprocal of the rate expression for R_p (Eq. 2) and rearranging gives the following expression:

$$1/R_p = k_t/k_p k'[TA][M] + \frac{k_t(k_0/k_i)[V^{5+}]}{k_p k'[TA][M^2]} \qquad (4)$$

Plots of $1/R_p$ versus $[V^{5+}]$ according to Eq. (4) are linear (Fig. 3).

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