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Polymerization of Methyl Methacrylate Initiated by Thiourea-V^{5+} Redox System

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ABSTRACT

Kinetics of the vinyl polymerization of methyl methacrylate initiated by V^{5+}-thiourea redox system were investigated in aqueous sulfuric acid in the temperature range of 35 to 50°C, and the rate of polymerization, V^{5+} disappearance, etc. were measured. From the results it was concluded that the polymerization reaction is initiated by an organic free radical arising from the V^{5+}-thiourea reaction and terminated by V^{5+} ions. The effects of certain organic solvents (water miscible) and salts on the rate of polymerization have been studied. The rate parameters have been evaluated.

INTRODUCTION

The kinetics and the mechanism of the vinyl polymerization initiated by redox systems have attracted the attention of several groups of workers [1-20]. Organic sulfur compounds coupled with a number of metal and nonmetal ions have proved to be potential initiators for a number of polymerizing systems. Bonvicini and Caldo [21] and

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Sugimura et al. [22] have used thiocompounds coupled with hydrogen peroxide for the aqueous polymerization of acrylonitrile. Mukherjee et al. [23] have used thiourea as the reductant with a number of oxidants such as ferric chloride, ethylene dibiguanide complex salts of tripositive silver (Ag^{3+}), hydrogen peroxide, persulfate, and bromate plus hydrochloric acid for polymerizing methyl methacrylate. Palit and co-workers [24] have reported the general features and kinetics of vinyl polymerization with Fe(III)-thiourea as the initiator. Sukla and Mishra [25] have reported the aqueous polymerization of acrylamide initiated by the acidified permanganate-thiourea redox system. Mishra and Gupta [26] have reported the aqueous polymerization of methacrylamide initiated by the acidified bromate-thiourea redox system. We have recently reported the aqueous polymerization of acrylonitrile initiated by Cr^{6+}-thiourea [27], V^{5+}-thiourea [28], and Mn^{3+}-thiourea [29] redox systems.

The present investigation includes the aqueous polymerization of methyl methacrylate initiated by V^{5+}-thiourea and V^{5+}-thioglycolic acid redox systems.

EXPERIMENTAL

Methyl methacrylate was washed with sodium hydroxide (5%) to remove the impurities, washed with water repeatedly and dried over anhydrous calcium chloride, and then distilled in the presence of nitrogen under vacuum and stored in a refrigerator. Ammonium metavanadate (A.R.), thioglycolic acid (A.R.), sulfuric acid (18 M: A.R.) were used. Water distilled thrice over alkaline permanganate and deionized by passing through a column of Biodeminrolit resin (Permutit, U.K.) was used to prepare all solutions.

Preparation of V(V) stock solutions, their estimations, etc. have already been described [12-14]. The polymerizations were heterogeneous with polymer precipitating continuously. Rates of polymerization were obtained gravimetrically, and rates of oxidant consumption were obtained by vanadometry on reaction mixtures arrested by the addition of excess standard ferrous ammonium sulfate solution.

RESULTS AND DISCUSSION

Methyl methacrylate was polymerized in aqueous sulfuric acid at 35 and 40°C in the presence of the redox systems V^{5+}-thiourea (TU) and V^{5+}-thioglycolic acid (TGA). A typical set of time conversion curves at 35-40°C and at various concentrations (0.0125 and 0.0875 M) of thiourea and at 35°C at various concentrations (0.01-0.125 M) of thioglycolic acid are shown in Figs. 1a and 1b.

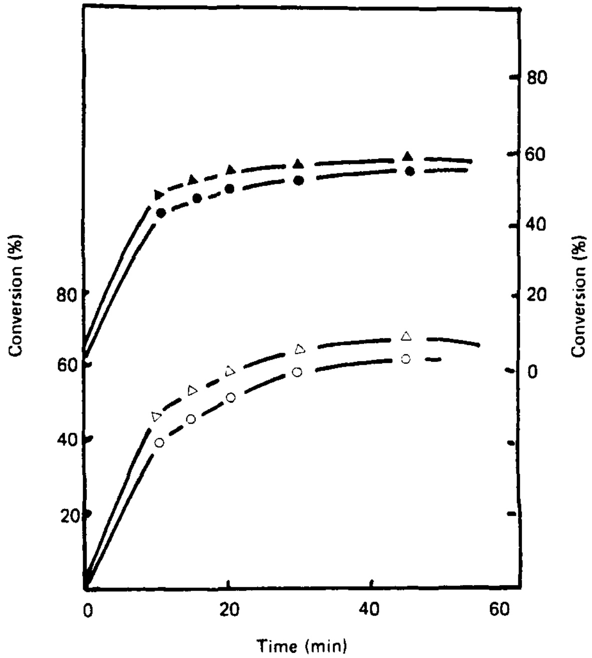

FIG. 1a. Time-conversion curves for different activator concentrations (TU): [V(V)] = 0.0125 M, [H$^+$] = 0.75 M, μ = 2.3 M, [MMA] = 0.09390 M. Time-conversion curves at [TU] = 0.0125 M: (○) 35°C, (△) 40°C. Time-conversion curves at [TU] = 0.0875 M: (●) 35°C, (▲) 40°C.

Rate of Polymerization (R_p)

The rate of polymerization, R_p, increased linearly with increasing monomer concentration (0.09388-0.2347 M) in the case of TU and (0.2347-0.469 M) in the case of TGA. The plots of R_p vs $[M]^2$ are linear and pass through the origin (Figs. 2a and 2b), and therefore the order with respect to [M] was 2 in both cases. The reciprocal plots of the rate ($1/R_p$) vs [V(V)] were linear with intercepts on the ordinate (Fig. 3). R_p increased linearly with an increase of thiourea concentration, but beyond 0.03 M the rate of polymerization decreases (Fig. 4). But in case of thioglycolic acid, the rate of polymerization

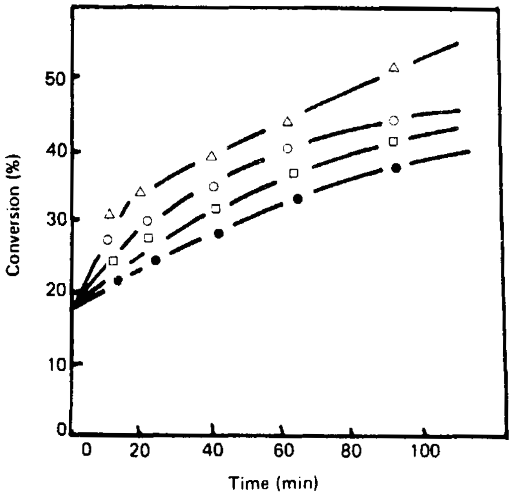

FIG. 1b. Time-conversion curves for different activator concentrations (TU): [V(V)] = 0.012 M, [H^+] = 0.975 M, [MMA] = 0.141 M, 35°C. (○) [TGA] = 0.01 M, (△) [TGA] = 0.02 M, (□) [TGA] = 0.05 M, (●) [TGA] = 0.125 M.

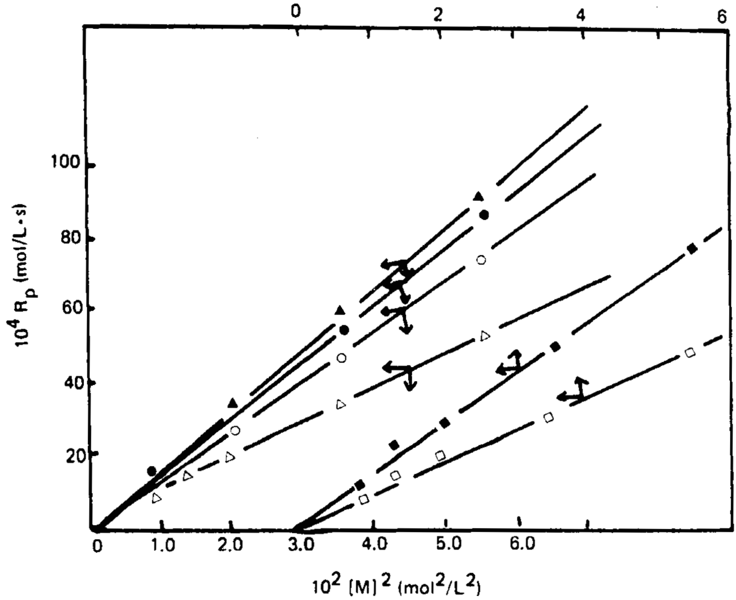

FIG. 2a. Variation of R_p with [Monomer]^2. [H^+] = 0.75 M, μ = 2.3 M, 40°C, [TU] = 0.025 M: (△) [V(V)] = 0.01 M, (○) [V(V)] = 0.015 M, (●) [V(V)] = 0.02 M, (▲) [V(V)] = 0.025 M. [TU] = 0.05 M: (□) [V(V)] = 0.01 M, (■) [V(V)] = 0.02 M.

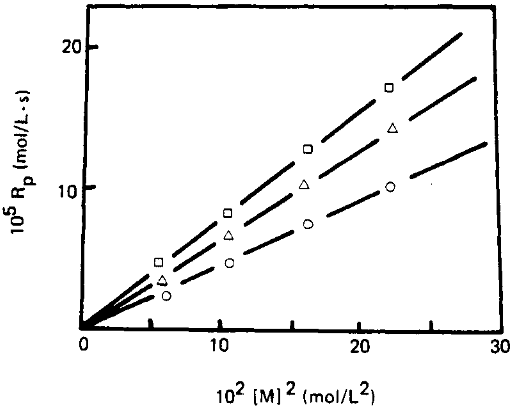

FIG. 2b. Variation of R_p with [Monomer]^2. [V(V)] = 0.0125 M, [TGA] = 0.0025 M, [H$^+$] = 0.575 M: (○) 40°C, (△) 45°C, (□) 50°C.

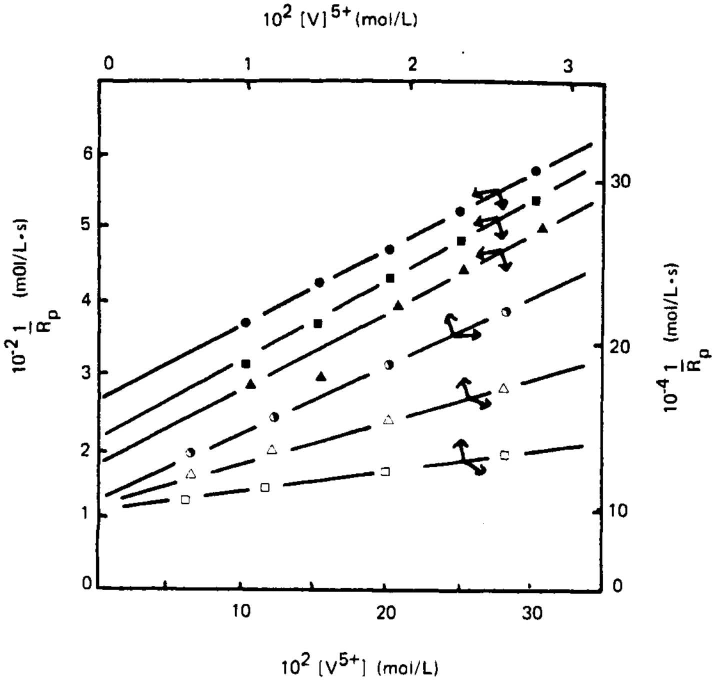

FIG. 3. Variation of $1/R_p$ with [V(V)]. [TU] = 0.025 M, [MMA] = 0.0939 M, μ = 3.1 M: (○) 30°C, (■) 35°C, (▲) 40°C. [TGA] = 0.0025 M, [MMA] = 0.1173 M, μ = 1.6 M: (◑) 40°C, (△) 45°C, (□) 50°C.

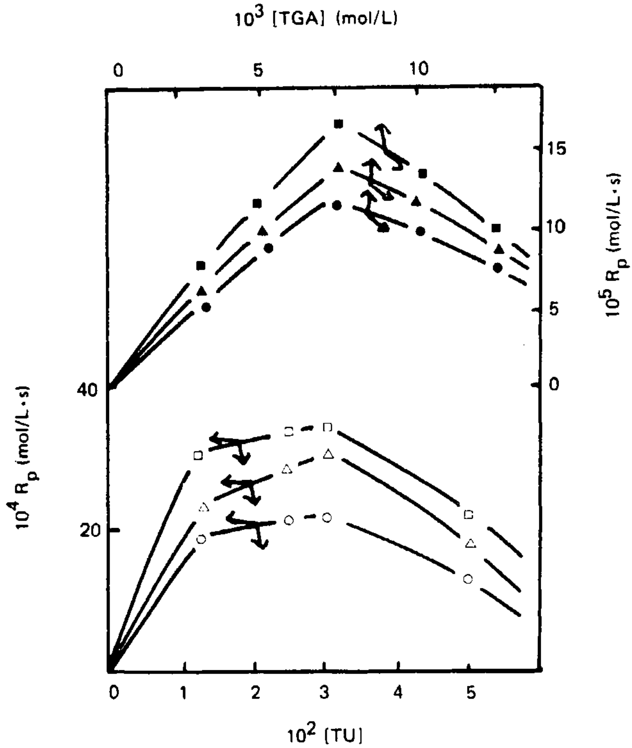

FIG. 4. Variation of R_p with [TU]. [V(V)] = 0.01 M, [H^+] = 0.75 M, μ = 2.3 M, [MMA] = 0.0939 M. (○) 30°C, (△) 35°C, (□) 40°C. Variation of R_p with [TGA]. [V(V)] = 0.0125 M, [MMA] = 0.1173 M, [H^+] = 0.575 M: (●) 40°C, (▲) 45°C, (■) 50°C.

increases up to 0.0075, but beyond this it decreases sharply. This decrease is probably due either to chain transfer or to the accompanying changes in polarity of the medium. Similar observations have been reported by Morgan [30], Josefowitz and Mark [31], Kolthoff and Harris [32], and Whitby et al. [33] for other systems.

R_p increased linearly with increasing [HSO_4^-], which includes equilibrium of the type

$$V(OH)_3^{2+} + HSO_4^- \rightleftharpoons V(OH)_3(HSO_4)^+$$

The species $V(OH)_3(HSO_4)^+$ is a more powerful oxidant than $V(OH)_3^{2+}$. This also indicates that bisulfate complexes of V^{5+} are

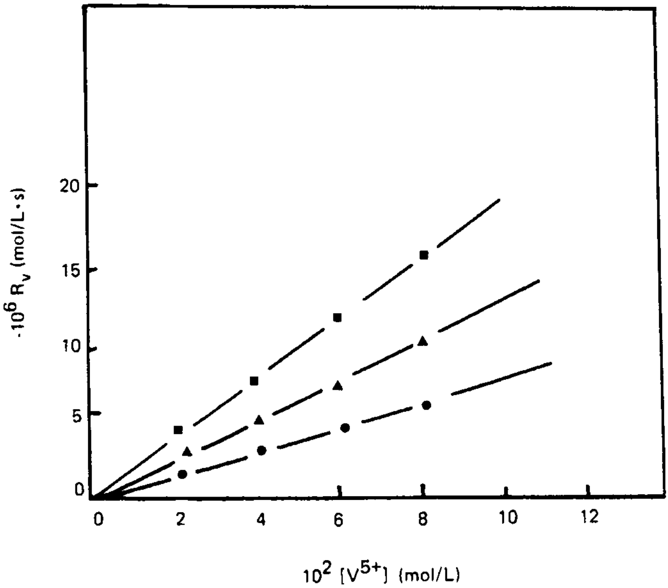

FIG. 5. Variation of $-R_V$ with [V(V)]. [TU] = 0.025 M, [MMA] = 0.9398 M, μ = 3.1 M: (●) 40°C, (▲) 45°C, (■) 50°C.

more effective initiators. Similar observations have been noticed by Nayak and co-workers in the polymerization of acrylonitrile initiated by the redox systems V^{5+}-cyclohexanone [12], V^{5+}-tartaric acid [14], V^{5+}-thiourea [28], Cr^{6+}-1,2-propane diol [16], Cr^{6+}-thiourea [27], Cr^{6+}-1-propanol [17], and by Santappa et al. [20] in the polymerization of acrylonitrile initiated by Co^{3+}.

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

The rate of metal ion disappearance ($-R_V$) in the case of thiourea was found to be independent of monomer concentration. The increase in $[V^{5+}]$ increased the rate. The plot of $-R_V$ vs $[V^{5+}]$ was linear, passing through the origin (Fig. 5), which indicates that the order with respect to V^{5+} is unity. The nondependence of $-R_V$ on [M] was also observed in the case of other redox systems (V^{5+}-cyclohexanone [12], V^{5+}-tartaric acid [14] V^{5+}-thiourea [28], V^{5+}-pinacol [34]), indicating that V^{5+} was not directly involved in the initiation step.

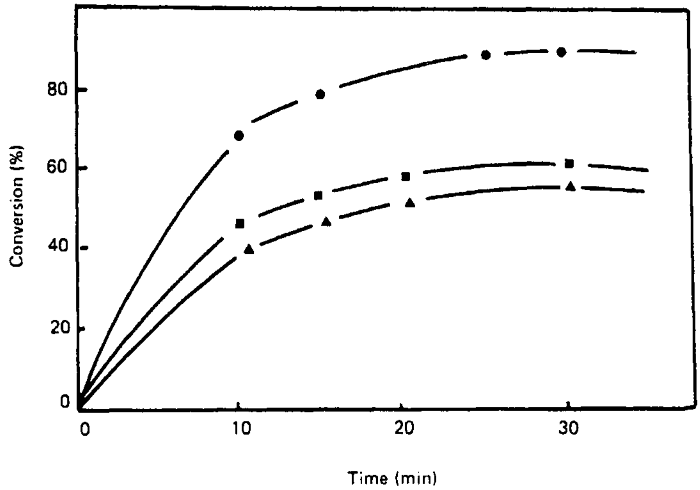

FIG. 6. Effect of 0.02 M inorganic salts: (▲) $MnSO_4$, (■) KCl, (●) NaF.

Rate Dependence on Additives

Addition of 5% (v/v) water-miscible organic solvents such as methanol, dimethylformamide, and formic acid tend to decrease the rate of polymerization as well as limiting conversion. Similar observations were noted by Kern and co-workers [35] and by us, and the explanation has been illustrated in our previous communications [12-19].

Effect of Inorganic Salts

The addition of small amounts of mono-monovalent (KCl) and bi-bivalent ($MnSO_4$) electrolytes to the system depress the rate and the maximum conversion (Fig. 6), possibly due to the resultant increase in the ionic strength of the medium. This is similar to our previous observations [12-19].

Effect of Complexing Agents

Addition of certain organic nitrogen compounds such as pyridine and piperidine to the system decreases the rate of polymerization. This might be due to 1) a change in pH of the medium due to the consumption of H^+ ions by the complexing reagents, and 2) a reduction in the activity of the initiator due to the coordination with the nitrogen ligand.

TABLE 1. Rate and Activation Parameters for the Polymerization of Methyl Methacrylate with Thiourea-V(V) Redox System

Temperature (°C)	k' × 10 L/mol/s [from $-R_v$ vs V(V)]	k_p/k_t	k_0/k_i
40	1.312	0.126	21.220
45	2.525	0.147	18.805
50	6.075	0.190	15.720

Effect of Surfactants. Addition of anionic surfactants (sodium laural sulfate) to the reaction mixture below and above CMC decreases the rate of polymerization. The retarding effect of the anionic surfactant may be explained by assuming specific ion pair binding of the cation V^{5+} with the anion RSO_4^- which might lower the rate of primary radical production. Alexander and co-workers [36] have assumed such ion pair binding between cationic surfactant and thiosulfate ions above and below CMC, leading to the formation of a complex which could be dissolved or dispersed by further addition of cations. Hence the rate is reduced.

Mechanism and Rate Law

Preliminary experiments carried out with V^{5+} and methyl methacrylate in sulfuric acid medium under deaerated conditions showed that no polymerization took place and there was no decrease in V^{5+} concentration. Of the various possible scheme examined, that of initiation by V^{5+} and $R^{\cdot}$ and termination by V^{5+} satisfied the experimental results. The detailed scheme was discussed in our previous communications [12-14]. The rate parameters and activation energies (Table 1) were evaluated there. The values of $E_p - E_t$ and $E_0 - E_i$ were computed to be 24.9 and 24.5 kJ/mol, respectively. The corresponding entropy of activation values were computed to be -183.1 and 285.9 J/K/mol, respectively.

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