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Vinyl Polymerization of Ethyl Acrylate Initiated by Tl^{3+}-Ascorbic Acid Redox System

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ABSTRACT

Thallium(III) perchlorate alone was found to be ineffective as an initiator for the vinyl polymerization of ethyl acrylate. However, in the presence of the activator ascorbic acid, the redox system Tl^{3+}-ascorbic acid was found to initiate polymerization. The kinetics of polymerization of ethyl acrylate initiated by the Tl^{3+}-ascorbic acid redox system was investigated in aqueous perchloric acid medium in the temperature range 55-70°C in the presence of oxygen. The rate of polymerization was evaluated by varying the concentrations of ethyl acrylate, Tl^{3+}, ascorbic acid, and perchlorid acid. The rate of polymerization was found to increase steadily with an increase of monomer concentration, Tl^{3+} concentration, ascorbic acid concentration, and perchloric acid concentration. The effects of additives such as organic solvents, different surfactants, and inhibitors on the initial rate of polymerization were investigated. Molecular weights and chain length of the purified polymer were determined by viscometry. Chain transfer with various solvents was studied and the chain transfer constants were calculated to be 0.13×10^4 for methanol, 0.43×10^4 for dioxane, and 0.69×10^4 for acetone.

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From the Arrhenius plot the overall activation energy was found to be 6.82 kcal/mol. A suitable kinetic scheme has been proposed and a rate equation has been derived.

INTRODUCTION

The mechanism of the oxidation of organic substrates by thallium(III) salts is fairly well established [1-5]. We recently carried out detailed kinetic investigations of vinyl polymerization of acrylonitrile initiated by thallium(III) perchlorate in aqueous perchloric acid medium [6]. Polymerization of ethyl acrylate could not be carried out following an identical procedure. The use of ascorbic acid as an activator in various redox systems used for the initiation of vinyl polymerization has attracted attention in recent years [7, 8]. As ethyl acrylate could not be polymerized by Tl^{3+} ions alone as initiator, it was thought interesting to investigate the feasibility of the Tl^{3+}-ascorbic acid redox system as an initiator for vinyl polymerization of this monomer. This redox system was found to be quite effective in initiating vinyl polymerization. The presence of dissolved oxygen in the reaction system, instead of inhibiting the polymerization rate, autocatalyzed it.

EXPERIMENTAL

Procedures for the preparation and estimation of thallium(III) perchlorate, for the purification of monomer and other chemicals, and for polymerization reactions are the same as those communicated earlier [6]. The values of the rate of polymerization (R_p) were determined gravimetrically.

Molecular weights of purified poly(ethyl acrylate) were determined by viscometry using a Ubbelohde suspended level dilution viscometer, and chain lengths were computed using the suitable Mark-Houwink-type equation.

RESULTS AND DISCUSSION

Effect of Monomer Concentration

The effect of monomer concentration on the rate of polymerization was studied by varying the concentration of ethyl acrylate in the range $0.92\text{-}4.61 \times 10^{-1}$ mol/L. The rate of polymerization was found to increase linearly with an increase of monomer concentration. The plot of R_p versus $[M]$ is linear, passing through the origin

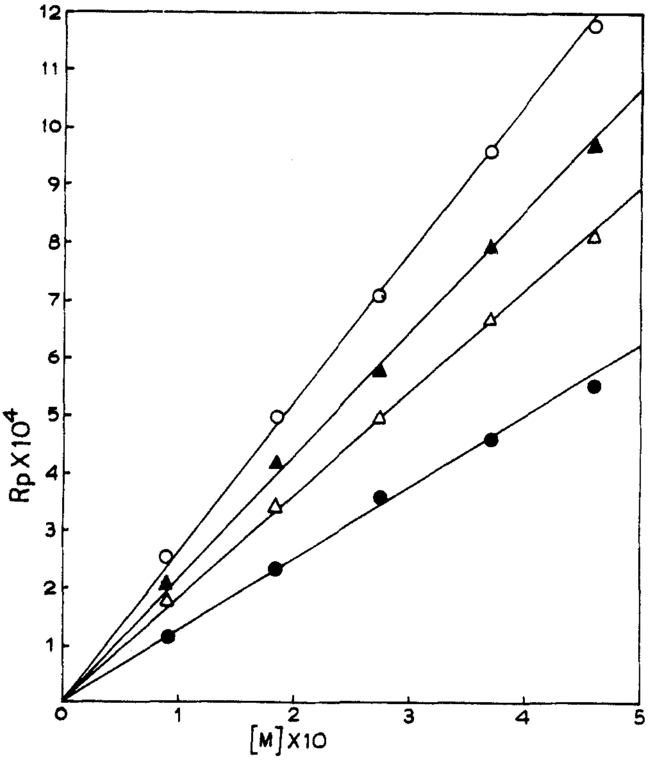

FIG. 1. Effect of monomer concentration on the rate of polymerization: [$HClO_4$] = 0.74 mol/L; [Tl^{3+}] = 4.08 × 10^{-3} mol/L; temperature = 70°C; time = 4 h. (○): [R] = 4.5 × 10^{-3} mol/L. (▲): [R] = 3.5 × 10^{-3} mol/L. (△): [R] = 2.5 × 10^{-3} mol/L. (●): [R] = 1.5 × 10^{-3} mol/L.

(Fig. 1) and indicating that the order of the reaction is unity with respect to monomer concentration. As the concentration of the monomer is increased, a large number of monomer units becomes available for the production of more free radicals which increase the rate of polymerization.

Effect of Initiator Concentration

The effect of thallium(III) perchlorate concentration on the rate of polymerization was studied by varying the concentration of the initiator in the range 4.08-20.40 × 10^{-3} mol/L. A progressive increase in the rate of polymerization was observed with an increase of Tl^{3+}

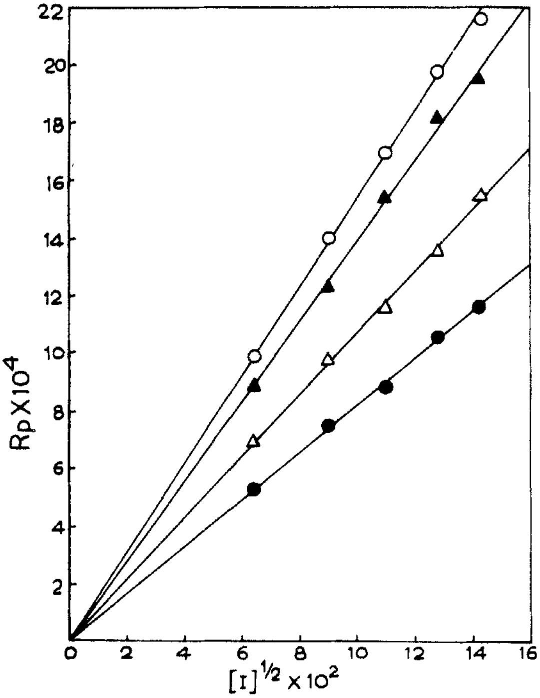

FIG. 2. Effect of initiator concentration on the rate of polymerization: [$HClO_4$] = 0.74 mol/L; [Monomer] = 4.61 × 10^{-1} mol/L; temperature = 70°C; time = 4 h. (○): [R] = 4 × 10^{-3} mol/L. (▲): [R] = 3 × 10^{-3} mol/L. (△): [R] = 2 × 10^{-3} mol/L. (●): [R] = 1 × 10^{-3} mol/L.

concentration. The plot of R_p versus $[I]^{1/2}$ is linear, passing through the origin (Fig. 2). This indicates the order of the reaction with respect to Tl^{3+} concentration to be 0.5.

Effect of Substrate Concentration

The effect of substrate concentration on the rate of polymerization was studied by varying the concentration of ascorbic acid in the range 1.00-4.00 × 10^{-3} mol/L. The rate of polymerization was found to increase with an increase of the substrate concentration [R]. The plot of R_p versus $[R]^{1/2}$ is linear, passing through the origin (Fig. 3), and indicating that the order of the reaction with respect to the substrate concentration is 0.5. A possible explanation

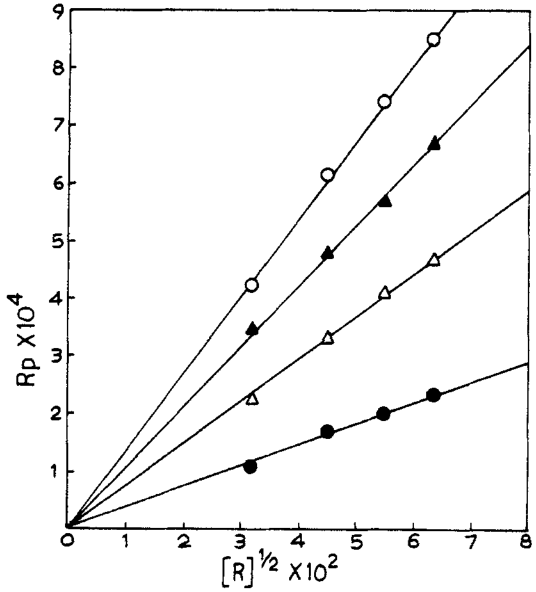

FIG. 3. Effect of substrate concentration on the rate of polymerization: [$HClO_4$] = 0.74 mol/L; [Tl^{3+}] = 4.08 × 10^{-3} mol/L; temperature = 70°C; time = 4 h. (○): [M] = 3.68 × 10^{-1} mol/L. (▲): [M] = 2.76 × 10^{-1} mol/L. (△): [M] = 1.84 × 10^{-1} mol/L. (●): [M] = 0.92 × 10^{-1} mol/L.

for this observation can be advanced by assuming that the reaction is initiated by organic free radicals produced by the interaction of Tl^{3+} with ascorbic acid. The production of these organic free radicals is facilitated at higher concentrations of ascorbic acid, thus accounting for the increase in the rate of polymerization.

Effect of Acid Concentration

Acid is essential for polymerization reactions initiated by thallium(III) perchlorate because perchlorate is hydrolyzed in aqueous medium and is subsequently converted to black thallic oxide. It is therefore of interest to observe the effect of acid concentration on the rate of polymerization. The perchloric acid concentration was varied in the range 0.34-0.74 mol/L. It was observed that the rate of polymerization increased progressively with an increase in perchloric acid concentration (Fig. 4). This may be due to the increased activity of thallium(III) perchlorate at high perchloric acid

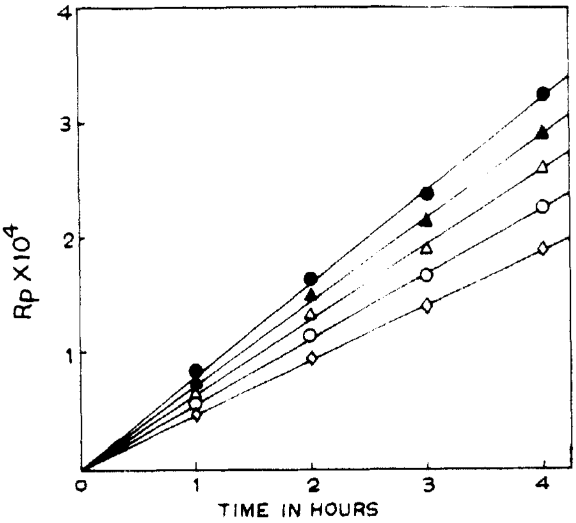

FIG. 4. Effect of acid concentration on the rate of polymerization: $[Tl^{3+}] = 4.08 \times 10^{-3}$ mol/L; $[M] = 2.76 \times 10^{-1}$ mol/L; $[R] = 2.00 \times 10^{-3}$ mol/L; temperature = 70°C. (●): $[HClO_4] = 0.74$ mol/L. (▲): $[HClO_4] = 0.64$ mol/L. (△): $[HClO_4] = 0.54$ mol/L. (○): $[HClO_4] = 0.44$ mol/L. (◇): $[HClO_4] = 0.34$ mol/L.

concentrations. A similar result was reported by Nayak et al. [5] in the case of oxidation of acetophenones initiated by thallium(III) acetate.

Effect of Temperature

The polymerization of ethyl acrylate initiated by the Tl^{3+}-ascorbic acid redox system was investigated in the temperature range 55-70°C. The rate of polymerization was found to increase with an increase in temperature (Fig. 5). This may be due to the increase in the activation energy and the greater rate of diffusion of the monomer into the active sites at high temperatures. From the Arrhenius plot of log R_p versus 1/T (Fig. 6), the overall activation energy was calculated to be 6.82 kcal/mol.

Effect of Various Solvents

The influence of various organic solvents on the rate of polymerization was studied. It was observed that addition of dioxane increased the rate of polymerization while methanol and acetone depressed it.

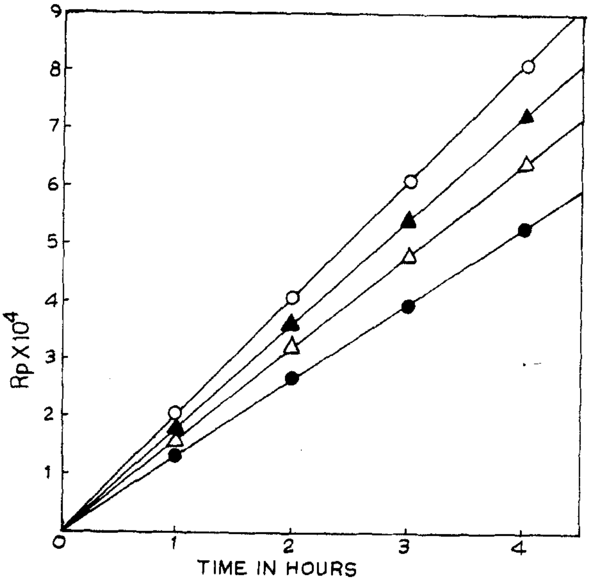

FIG. 5. Effect of temperature on the rate of polymerization: $[HClO_4] = 0.74$ mol/L; $[Tl^{3+}] = 4.08 \times 10^{-3}$ mol/L; $[M] = 4.61 \times 10^{-1}$ mol/L; $[R] = 2.5 \times 10^{-3}$ mol/L. (○): Temperature = 70°C. (▲): Temperature = 65°C. (△) Temperature = 60°C. (●) Temperature = 55°C.

In the case of dioxane an increase of solvent concentration increased the rate of polymerization (Fig. 7). In the case of acetone and methanol a decrease in the rate of polymerization with an increase in solvent concentration was observed (Figs. 8 and 9). The different solvents studied were found to follow the following sequence: dioxane > without any solvent > methanol > acetone.

The monomer forms a heterogeneous system with the aqueous medium. Dioxane is miscible with water in all proportions and acts as a better solvent for the monomer. As such, addition of dioxane to the polymerization medium results in an increase in the rate of polymerization.

The decrease in rate of polymerization observed upon addition of acetone and methanol may be due to a decrease in the area of shielding of a strong hydration layer in the aqueous medium, resulting in the termination of the growing chain. This may also be due to the increase in the regulated rate of production of primary radicals caused by the solvents which, under the existing experimental conditions, renders the termination rate relatively fast as compared to the rate of growth of the polymer chain. This is in agreement with the views of Kern et al. [9].

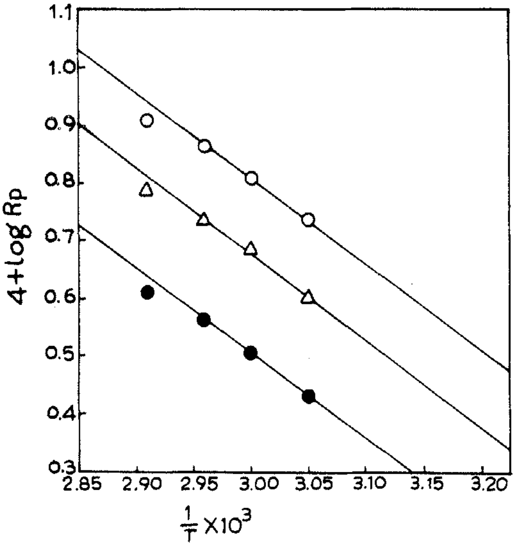

FIG. 6. Arrhenius plot of log R_p vs 1/T. (○): 4 h. (△): 3 h. (●): 2 h.

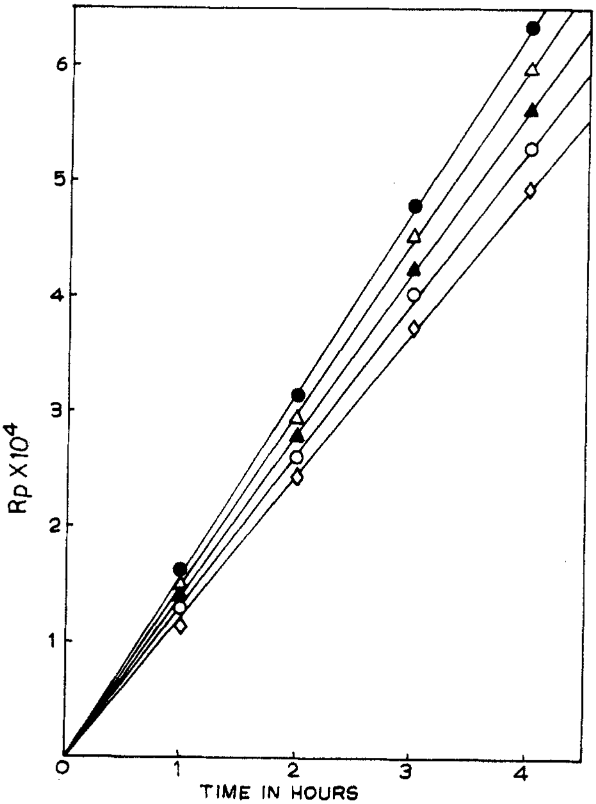

FIG. 7. Effect of the solvent dioxane on the rate of polymerization: [$HClO_4$] = 0.74 mol/L; [Tl^{3+}] = 4.08 × 10^{-3} mol/L; [M] = 2.76 × 10^{-1} mol/L; [R] = 2.00 × 10^{-3} mol/L; Temperature = 70°C. (●): [dioxane] = 14.62 × 10^{-1} mol/L. (△): [dioxane] = 11.70 × 10^{-1} mol/L. (▲): [dioxane] = 8.77 × 10^{-1} mol/L. (○): [dioxane] = 5.85 × 10^{-1} mol/L. (◇): [dioxane] = 2.92 × 10^{-1} mol/L.

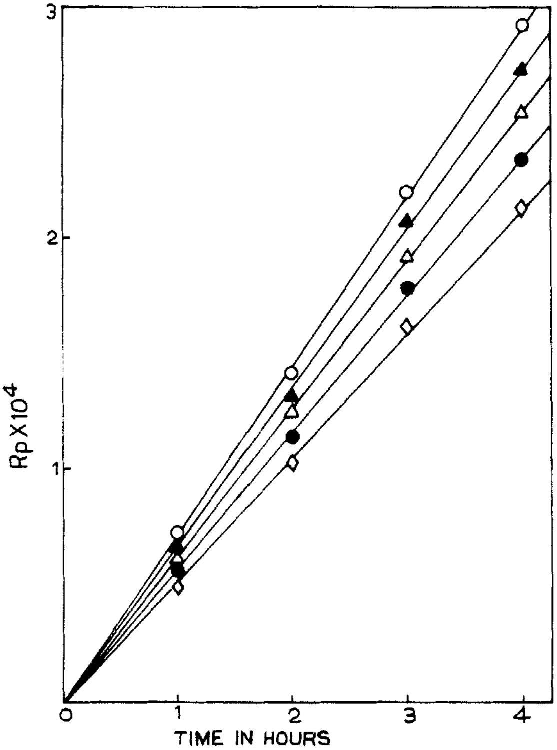

FIG. 8. Effect of the solvent acetone on the rate of polymerization: [$HClO_4$] = 0.74 mol/L; [Tl^{3+}] = 4.08 × 10^{-3} mol/L; [M] = 2.76 × 10^{-1} mol/L [R] = 2.00 × 10^{-3} mol/L; temperature = 70°C. (○): [acetone] = 3.41 × 10^{-1} mol/L. (▲): [acetone] = 6.82 × 10^{-1} mol/L. (△): [acetone] = 10.23 × 10^{-1} mol/L. (●): [acetone] = 13.64 × 10^{-1} mol/L. (◇): [acetone] = 17.05 × 10^{-1} mol/L.

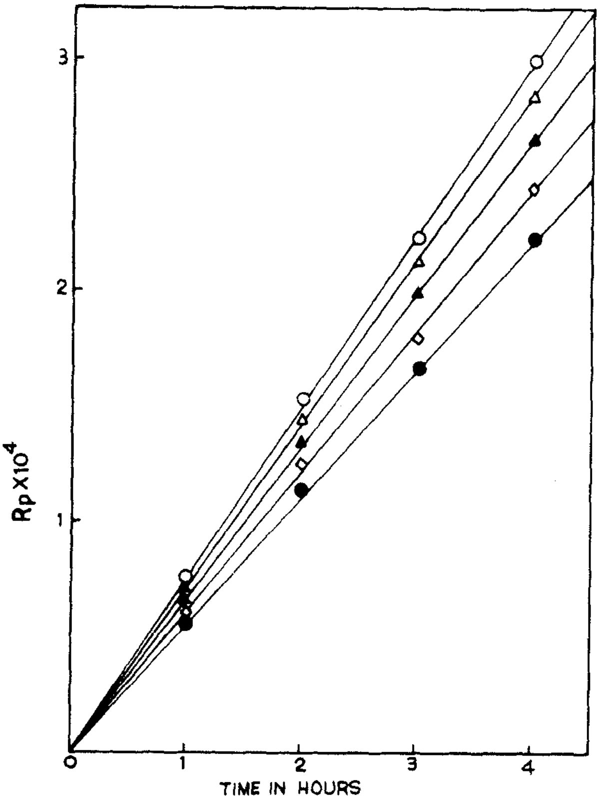

FIG. 9. Effect of the solvent methanol on the rate of polymerization: [$HClO_4$] = 0.74 mol/L; [Tl^{3+}] = 4.08 × 10^{-3} mol/L; [M] = 2.76 × 10^{-1} mol/L; [R] = 2.00 × 10^{-3} mol/L; temperature = 70°C. (○): [methanol] = 6.21 × 10^{-1} mol/L. (△): [methanol] = 12.42 × 10^{-1} mol/L. (▲): [methanol] = 18.63 × 10^{-1} mol/L. (◇): [methanol] = 24.84 × 10^{-1} mol/L. (●): [methanol] = 31.05 × 10^{-1} mol/L.

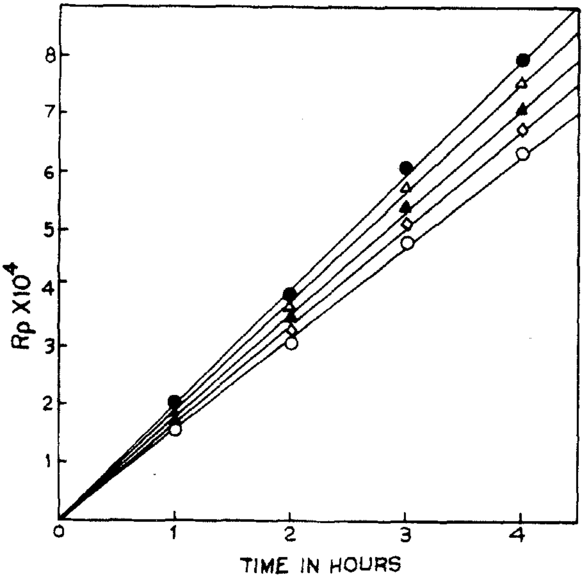

FIG. 10. Effect of the inhibitor hydroquinone on the rate of polymerization: [$HClO_4$] = 0.74 mol/L; [Tl^{3+}] = 4.08 × 10^{-3} mol/L; [M] = 4.61 × 10^{-1} mol/L; [R] = 2.50 × 10^{-3} mol/L; temperature = 70°C. (●): [hydroquinone] = 0.2 × 10^{-3} mol/L. (△): [hydroquinone] = 0.4 × 10^{-3} mol/L. (▲): [hydroquinone] = 0.6 × 10^{-3} mol/L. (◇): [hydroquinone] = 0.8 × 10^{-3} mol/L. (○): [hydroquinone] = 1.0 × 10^{-3} mol/L.

Effect of Inhibitors

The addition of such inhibitors as hydroquinone and picryl chloride to the reaction mixture greatly suppressed the rate of polymerization (Figs. 10 and 11), suggesting a free radical mechanism for the reaction. The inhibiting efficiency of picryl chloride was found to be greater than that of hydroquinone. In either case an increase in inhibitor concentration decreased the rate of polymerization. As the concentration of the inhibitor increases, it traps more and more free radicals, thereby decreasing the rate of polymerization.

Effect of Surfactants

The effect of cationic (CTABr), anionic (NaLS), and nonionic (Triton-X-100) surfactants on the rate of polymerization was investigated. Anionic micelles of sodium lauryl sulfate increased the rate

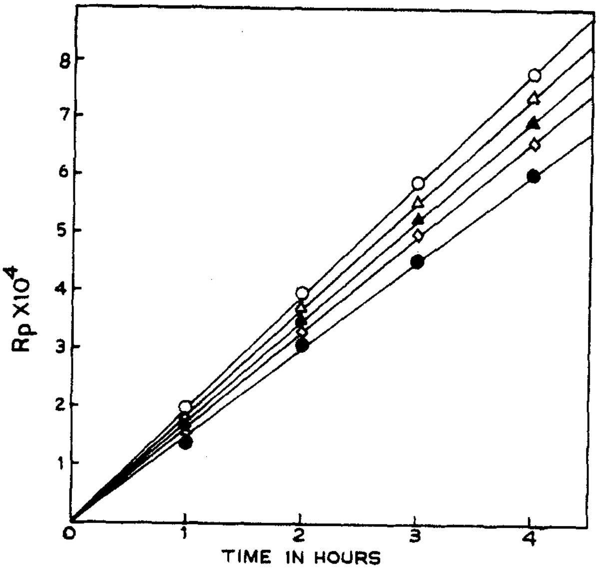

FIG. 11. Effect of the inhibitor picryl chloride on the rate of polymerization: $[HClO_4] = 0.74$ mol/L; $[Tl^{3+}] = 4.08 \times 10^{-3}$ mol/L; $[M] = 4.61 \times 10^{-1}$ mol/L; $[R] = 2.50 \times 10^{-3}$ mol/L; temperature = 70°C. (○): [picryl chloride] = 0.2×10^{-3} mol/L. (△): [picryl chloride] = 0.4×10^{-3} mol/L. (▲): [picryl chloride] = 0.6×10^{-3} mol/L. (◇): [picryl chloride] = 0.8×10^{-3} mol/L. (●): [picryl chloride] = 1.0×10^{-3} mol/L.

of polymerization. This increasing trend was maintained up to the critical micelle concentration (CMC). At CMC the rate of polymerization was at a maximum and at concentrations above CMC a decreasing trend was noticed (Fig. 12). With a cationic surfactant (CTABr) the rate of polymerization decreased and a decreasing trend was maintained with an increase in surfactant concentration (Fig. 13). The rate of polymerization was not influenced by the nonionic surfactant (Triton-X-100). The hydrophobic interations and the electrostatic attraction are chiefly responsible for the spectacular rate enhancement or inhibition exhibited by the micelles of the surfactants [10-12].

Chain Transfer with Different Solvents

The molecular weights of poly(ethyl acrylate) were determined by viscometry using the suitable Mark-Houwink-type equation. The

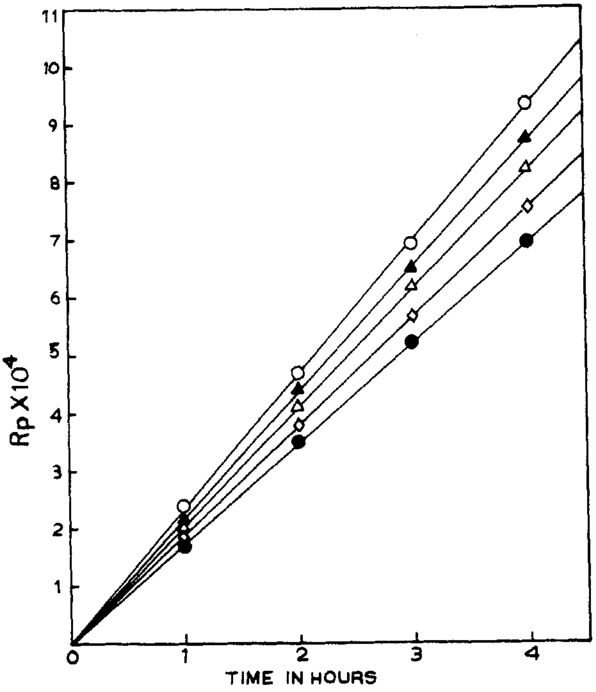

FIG. 12. Effect of the anionic surfactant (NaLS) on the rate of polymerization: [$HClO_4$] = 0.74 mol/L; [Tl^{3+}] = 4.08×10^{-3} mol/L; [M] = 4.61×10^{-1} mol/L; [R] = 2.50×10^{-3} mol/L; temperature = 70°C. (○): [NaLS] = 8.10×10^{-3} mol/L. (▲): [NaLS] = 6.30×10^{-3} mol/L. (△): [NaLS] = 5.00×10^{-3} mol/L. (◇): [NaLS] = 10.00×10^{-3} mol/L. (●): [NaLS] = 11.25×10^{-3} mol/L.

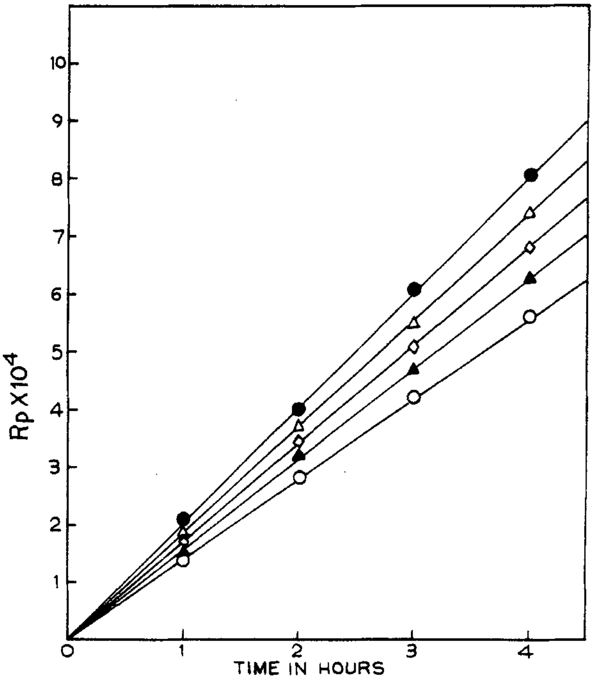

FIG. 13. Effect of the cationic surfactant (CTABr) on the rate of polymerization: [$HClO_4$] = 0.74 mol/L; [Tl^{3+}] = 4.08 × 10^{-3} mol/L; [M] = 4.61 × 10^{-1} mol/L; [R] = 2.50 × 10^{-3} mol/L; temperature = 70°C. (●): [CTABr] = 0.7 × 10^{-3} mol/L. (△): [CTABr] = 0.8 × 10^{-3} mol/L. (◇): [CTABr] = 0.92 × 10^{-3} mol/L. (▲): [CTABr] = 1.2 × 10^{-3} mol/L. (○): [CTABr] = 1.4 × 10^{-3} mol/L.

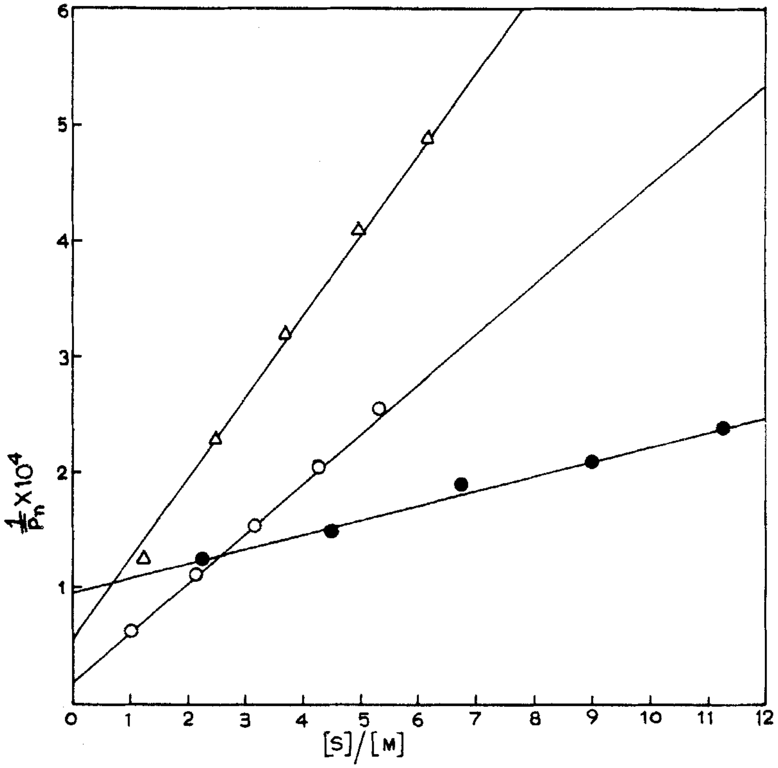

FIG. 14. Chain transfer with different solvent. (○): Solvent, dioxane. (△): Solvent, acetone. (●): Solvent, methanol.

molecular weights of polymers formed with different solvents were determined, and the degree of polymerization ($\bar{P}_n$) was calculated in each case. It was observed that an increase of solvent concentration decreased the molecular weight of the polymer. This may be due to termination of the polymer via chain transfer. The chain transfer constant (C_s) for various solvents was evaluated by using

$$\frac{1}{\bar{P}_n} = \left[\frac{1}{\bar{P}_n}\right]_0 + C_s\frac{[S]}{[M]}$$

where [S] = concentration of the solvent, [M] = concentration of the monomer, and $[1/\bar{P}_n]_0$ = a constant.

A plot of $1/\overline{P}_n$ versus $[S]/[M]$ gives a straight line for each solvent (Fig. 14), and the slope of the line directly gives the value of the chain transfer constant for the particular solvent. The chain transfer constant was calculated to be 0.13×10^4 for methanol, 0.43×10^4 for dioxane, and 0.69×10^4 for acetone.

MECHANISM

From the proportionalities obtained between the measurable parameters and variables, a reaction scheme involving the initiation by organic free radical produced by the interaction of Tl^{3+} with ascorbic acid and termination by mutual combination of the growing chains has been suggested.

(i) Production of organic free radical:

$$Tl^{3+} + R \xrightarrow{k_d} Tl^{2+} + R^{\bullet}$$

where R = ascorbic acid and $R^{\bullet}$ = organic free radical.
(ii) Initiation:

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

where M = the monomer and $M^{\bullet}$ = monomer free radical.
(iii) Propagation:

$$\begin{array}{l} M^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet} \\ \vdots \\ M_{n-1}^{\bullet} + M \xrightarrow{k_p} M_n^{\bullet} \end{array}$$

(iv) Termination:

$$M_n^{\bullet} + M_n^{\bullet} \xrightarrow{k_t} \text{polymer}$$

Assuming steady state for the free radicals, the rate laws have been derived as follows:

$$k_d[Tl^{3+}][R] = k_i[R^{\bullet}][M]$$

or

$$[R^{\bullet}] = \frac{k_d[Tl^{3+}][R]}{k_i[M]}$$

Again,

$$k_i[R^{\bullet}][M] = k_t[M_n^{\bullet}]^2$$

or

$$[M_n^{\bullet}]^2 = \frac{k_i}{k_t}[R^{\bullet}][M]$$

Substituting the value of $[R^{\bullet}]$ in the above equation:

$$[M_n^{\bullet}] = [\frac{k_d}{k_t}]^{1/2}[I]^{1/2}[R]^{1/2}$$

$$R_p = k_p[M][M_n^{\bullet}]$$

or

$$R_p = k_p\left[\frac{k_d}{k_t}\right]^{1/2}[M][I]^{1/2}[R]^{1/2}$$

Plots of R_p versus $[M]$ (Fig. 1), R_p versus $[I]^{1/2}$ (Fig. 2) and R_p versus $[R]^{1/2}$ are linear, passing through the origin, which confirms the validity of the above reaction scheme.

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