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Vinyl Polymerization of Acrylonitrile Initiated by Thallium(III) Ions in Solution

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ABSTRACT

Polymerization of acrylonitrile initiated by thallium(III) perchlorate was investigated in aqueous perchloric acid medium in the temperature range 55-70°C. The rate of polymerization was evaluated by varying the concentrations of monomer, initiator, and perchloric acid. The rate of polymerization was found to increase steadily with an increase of monomer concentration. The effect of solvents; micelles of cationic, anionic, and nonionic surfactants; and inhibitors on the rate of polymerization was also studied. Molecular weights and chain lengths of purified polyacrylonitrile were determined by viscometry. The chain transfer constants for the monomer (C_M) and that for the solvent dioxane (C_S) were calculated to be 1.7×10^4 and 1.6×10^4, respectively. From the Arrhenius plot, the overall activation energy was found to be 13.2 kcal/mol. A suitable kinetic scheme has been proposed and a rate equation has been derived.

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INTRODUCTION

Oxidation studies involving thallium(III) acetate were first reported by Meyer [1] as early as 1903. Later on thallium(III) acetate as well as other carboxylate salts were also used for the oxidation of phenols [2], olefins [3-9] and organomercuric compounds [10, 11]. South et al. [12] and Oullette et al. [13] have reported the oxidation of certain ring compounds using thallium(III) acetate. The mechanism of oxidation of organic substrates by thallium(III) salts has been fairly well established [14-18]. The use of thallium(III) salts as catalysts for vinyl polymerization has been scant [19, 20]. A survey of the literature reveals that detailed studies involving thallium(III) salts as an initiator of vinyl polymerization has not been reported until now. This communication reports for the first time a detailed study on the polymerization of acrylonitrile initiated by thallium(III) perchlorate.

EXPERIMENTAL

Thallium(III) perchlorate was prepared by dissolving thallium(III) oxide (B.D.H., Analar) in a minimum amount of perchloric acid (E. Merck, GR., 60%) at 75°C and thallium(III) perchlorate crystallized upon cooling. The crystals were filtered, washed with ether, and vacuum dried. Thallium(III) perchlorate solution was prepared by dissolving a calculated amount of thallium(III) perchlorate in a known volume of standard perchloric acid. The thallium(III) concentration was estimated titrimetrically by the iodide-thiosulfate analytical procedure [12].

Acrylonitrile was washed with sodium hydroxide solution (5%) and orthophosphoric acid solution (3%) to remove the inhibitor and basic impurities, respectively. It was then washed well with water, dried over anhydrous calcium chloride and distilled in the presence of nitrogen under reduced pressure. The middle fraction was stored at 5°C in a refrigerator and used for the experiments. Water distilled twice over alkaline permanganate and deionized by passing through a column of Biodeminrolit resin (Permutit Co., U.K.) was used to prepare all solutions. Nitrogen used for deaeration of the experimental system was purified by passing through several columns of Fieser solution, a column of saturated lead acetate solution, a wash bottle containing distilled water, and finally bubbling through the monomer.

Polymerization reactions were carried out following identical procedures as described earlier [21]. The values of the rate of polymerization (R_p) were determined gravimetrically.

Molecular weights of purified polyacrylonitrile 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

The kinetics of aqueous polymerization of acrylonitrile initiated by thallium(III) perchlorate was investigated in perchloric acid medium. Variables studied included monomer concentrations, thallium(III) concentrations, acid concentrations, temperature, different surfactants, and different solvents. The molecular weights of polyacrylonitrile were determined by viscometry.

Effect of Monomer Concentration

The effect of monomer concentration on the rate of polymerization was studied by varying the concentration of acrylonitrile from 3.75 to 30.00×10^{-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) and thus indicating the order of the reaction to be unity with respect to monomer concentration.

Effect of Initiator Concentration

The effect of initiator concentration on the rate of polymerization was studied by varying the concentration of the initiator from 2.18 to 17.48×10^{-3} mol/L at fixed concentrations of all other reagents. A progressive increase in the rate of polymerization was observed with an increase of the thallium(III) 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 the initiator concentration to be 0.5.

Effect of Acid Concentration

The polymerization reaction was carried out in aqueous perchloric acid medium. The acid concentration was varied from 0.64 to 1.14 mol/L at fixed concentrations of all other reagents. A progressive increase in the rate of polymerization was observed with an increase of perchloric acid concentration (Fig. 3). The increase in the rate of polymerization with an increasing concentration of the perchloric acid might be due to the increased reactivity of thallium(III) perchlorate at high perchloric acid concentration. A similar result has been reported by Nayak et al. [17] in the case of oxidation of acetophenone by thallium(III) acetate.

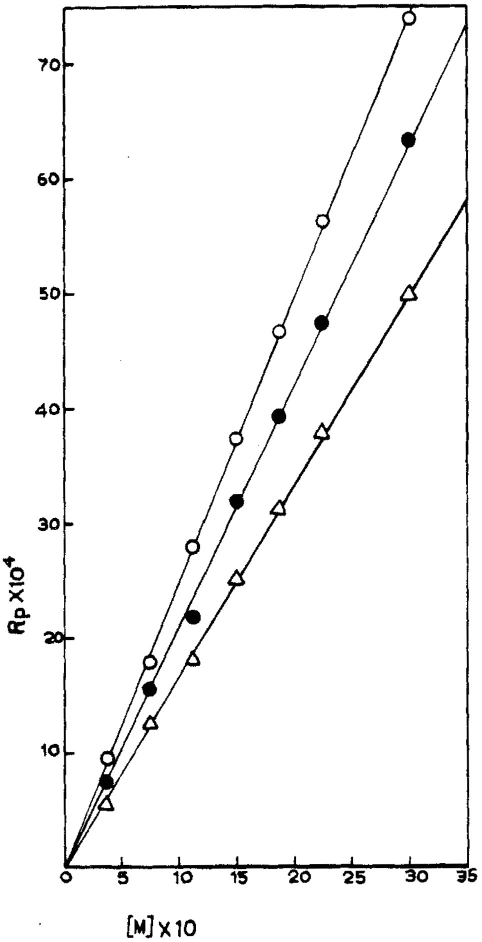

FIG. 1. Effect of monomer concentration on the rate of polymerization: acid concentration = 1.085 mol/L; temperature = 70° C; dioxane concentration = 5.85×10^{-1} mol/L; time = 4 h. (○): $[Tl^{3+}] = 17.48 \times 10^{-3}$ mol/L. (●): $[Tl^{3+}] = 13.11 \times 10^{-3}$ mol/L. (△): $[Tl^{3+}] = 8.74 \times 10^{-3}$ mol/L.

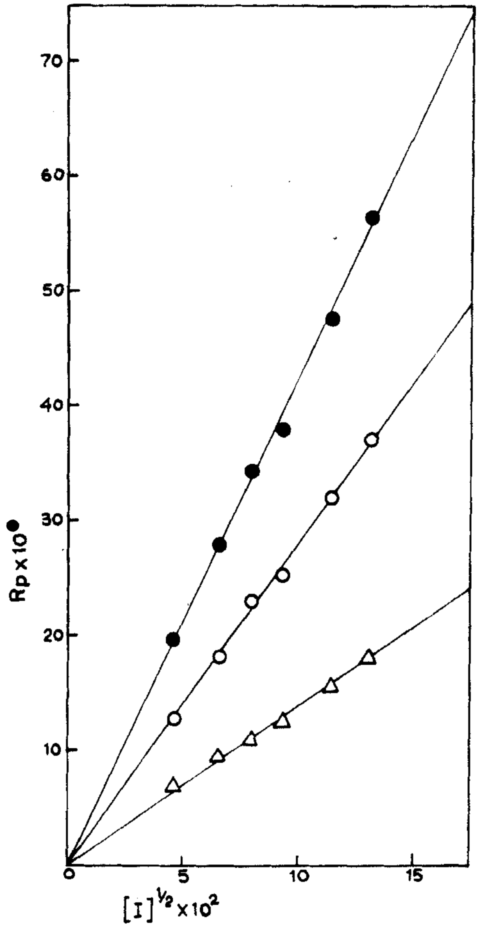

FIG. 2. Effect of initiator concentration on the rate of polymerization: acid concentration = 1.085 mol/L; temperature = 70° C; dioxane concentration = 5.85×10^{-1} mol/L; time = 4 h. (●): [AN] = 22.5×10^{-1} mol/L. (○): [AN] = 15.0×10^{-1} mol/L. (△): [AN] = 7.5×10^{-1} mol/L.

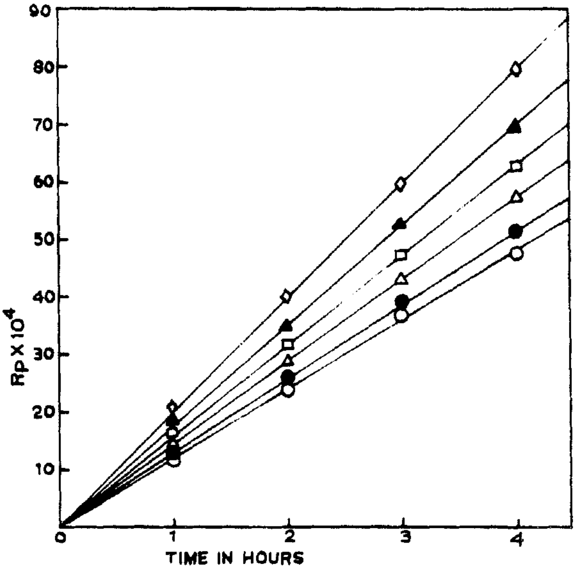

FIG. 3. Effect of acid concentration on the rate of polymerization: monomer concentration = 7.5×10^{-1} mol/L; initiator concentration = 2.18×10^{-3} mol/L; dioxane concentration = 5.85×10^{-1} mol/L; temperature = 70°C. (◇): [$HClO_4$] = 1.14 mol/L. (▲): [$HClO_4$] = 1.04 mol/L. (□): [$HClO_4$] = 0.94 mol/L. (△): [$HClO_4$] = 0.84 mol/L. (●): [$HClO_4$] = 0.74 mol/L. (○): [$HClO_4$] = 0.64 mol/L.

Effect of Temperature

The polymerization of acrylonitrile initiated by thallium(III) perchlorate was investigated in the temperature range 55-70°C, keeping the concentrations of all other reagents constant. The rate of polymerization was found to increase progressively with the rise in temperature (Fig. 4). This might be due to the following reasons: 1) the increase in the activation energy at high temperatures, 2) the enhancement of the rate of diffusion of monomer into the active sites with the rise in temperature and, 3) the increase in the rate of propagation of the polymer chain at high temperature.

From the Arrhenius plot of log R_p versus 1/T (Fig. 5), the overall activation energy (E_a) was computed to be 13.2 kcal/mol. The energy of initiation, E_d, was calculated by using

$$E_d = 2E_a - (2E_p - E_t)$$

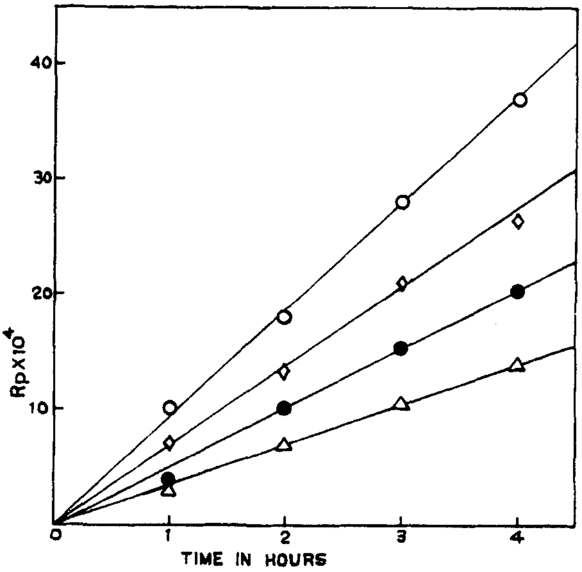

FIG. 4. Effect of temperature on the rate of polymerization: acid concentration = 1.085 mol/L; monomer concentration = 15.0 10^{-1} mol/L; initiator concentration = 17.48 × 10^{-3} mol/L; dioxane concentration = 5.85 × 10^{-1} mol/L. (○): Temperature = 70°C. (◇): Temperature = 65°C. (●): Temperature = 60°C. (△): Temperature = 55°C.

where E_p is the energy of propagation and E_t is the energy of termination. Using the value of $E_p - \frac{1}{2}E_t$ = 4-5 kcal/mol given by Tobolsky [22], the energy of initiation was found to be 17.4 kcal/mol.

Effect of Polymerization Medium

The reaction medium plays an important role in the vinyl polymerization of acrylonitrile initiated by thallium(III) perchlorate. Different solvents were added to the reaction mixture, and their effect on rate of polymerization was studied. The order of the solvents as far as the rate of polymerization is concerned follows the following sequence (Fig. 6): dioxane > acetone > methanol.

The variation of rate of polymerization with the use of different solvents could be due to the difference in either of the following factors: 1) capability of the solvent to dissolve the monomer in the polymerization medium, 2) formation of solvent radical from the primary radical species of the initiating system, 3) contribution of

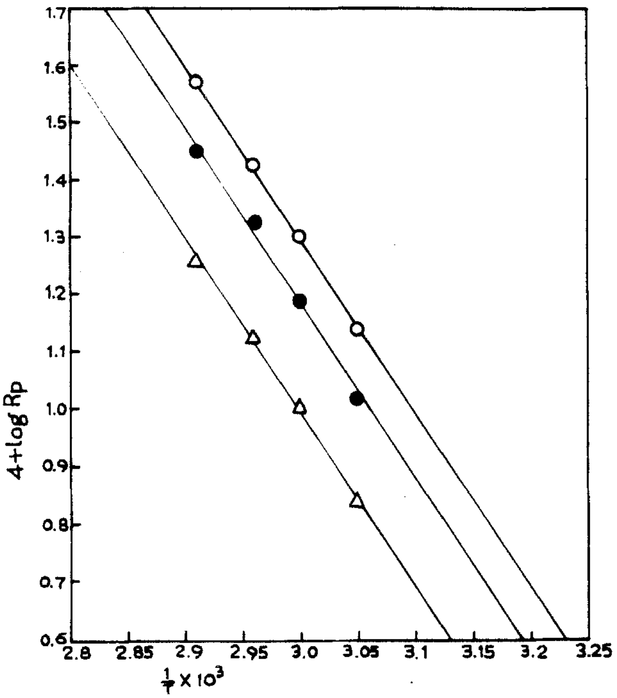

FIG. 5. Arrhenius plot of log R_p versus 1/T. (○): 4 h. (●): 3 h. (△): 2 h.

the solvent radical in activation of the monomer, 4) termination of the polymer via chain transfer. Out of the above factors, the first three favor polymerization whereas the last factor adversely affects polymerization.

Effect of Dioxane Concentration

Monomer forms a heterogeneous system with aqueous solution. 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 effect of dioxane concentration on the rate of polymerization was studied by varying the concentration of dioxane in the range 2.92-14.62 × 10^{-1} mol/L at fixed concentrations of all other reagents. The rate of polymerization was found to increase with increasing the dioxane concentration from 2.92 to 5.85 × 10^{-1} mol/L,

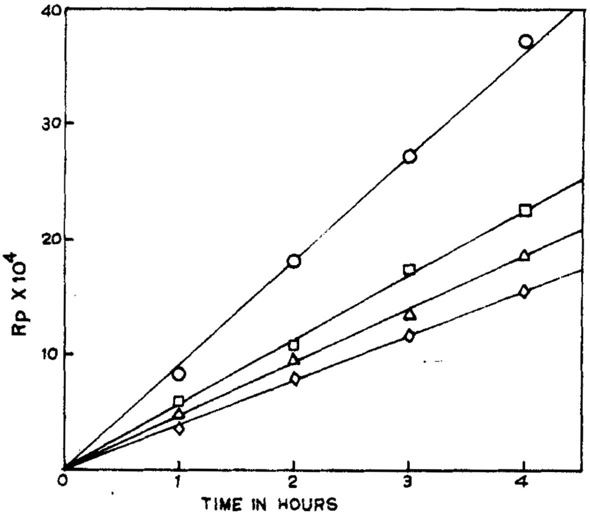

FIG. 6. Effect of various solvents on the rate of polymerization: acid concentration = 1.085 mol/L; monomer concentration = 15.0 10^{-1} mol/L; initiator concentration = 17.48 × 10^{-3} mol/L; solvent concentration = 5% v/v; temperature = 70°C. (○): Dioxane. (□): No solvent. (△): Acetone. (◇): Methanol.

and above this concentration the rate decreased continuously (Fig. 7). The decrease of the rate of polymerization beyond 5.85 × 10^{-1} mol/L of dioxane concentration might be due to the fact that the solvent radicals formed participate in the termination step.

Effect of Inhibitor Concentration

The effect of different inhibitors such as hydroquinone and picryl chloride on the rate of polymerization was studied at fixed concentrations of all other reagents. From the results it was observed that the rate of polymerization was greatly suppressed in the presence of either inhibitor (Figs. 8 and 9). It was observed that the inhibiting efficiency of picryl chloride was more than that of hydroquinone. The data also indicate that the extent of inhibition increases with an increase in the concentration of the inhibitor. As the concentration of the inhibitor increases, it traps more and more free radicals, thereby decreasing the rate of polymerization.

Effect of Surfactants

The rate of polymerization has been investigated in the presence of cationic (CTABr), anionic (NaLS), and nonionic (Triton X-100)

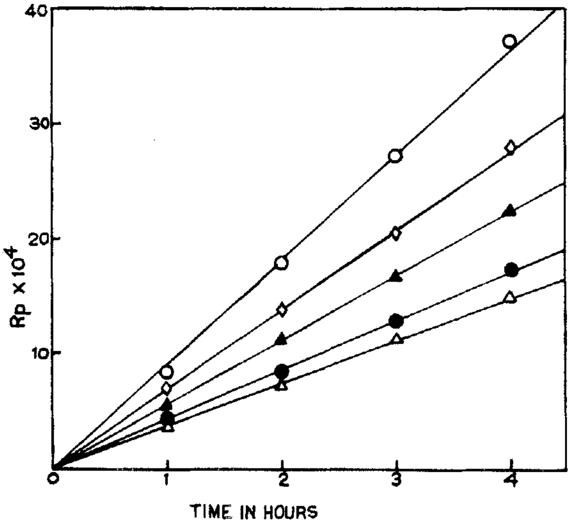

FIG. 7. Effect of dioxane concentration on the rate of polymerization: acid concentration = 1.085 mol/L; monomer concentration = 15.0×10^{-1} mol/L; initiator concentration = 17.48×10^{-3} mol/L; temperature = 70°C. (○): [dioxane] = 5.85×10^{-1} mol/L. (◇): [dioxane] = 8.77×10^{-1} mol/L. (▲): [dioxane] = 11.7×10^{-1} mol/L. (●): [dioxane] = 14.62×10^{-1} mol/L. (△): [dioxane] = 2.92×10^{-1} mol/L.

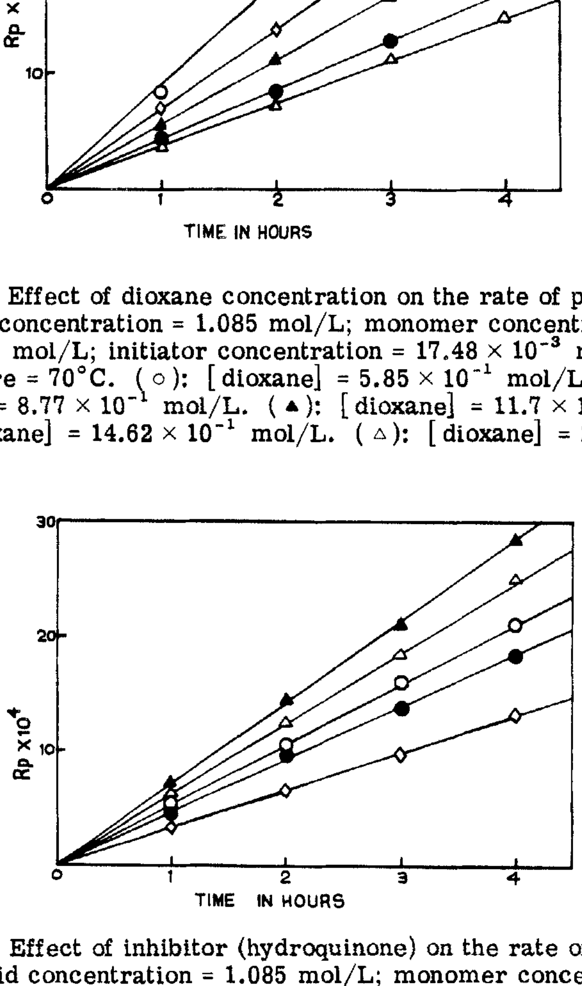

FIG. 8. Effect of inhibitor (hydroquinone) on the rate of polymerization: acid concentration = 1.085 mol/L; monomer concentration = 15.0×10^{-1} mol/L; initiator concentration = 17.48×10^{-3} mol/L; dioxane concentration = 5.85×10^{-1} mol/L; temperature = 70°C. (▲): [hydroquinone] = 0.2×10^{-3} mol/L. (△): [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.

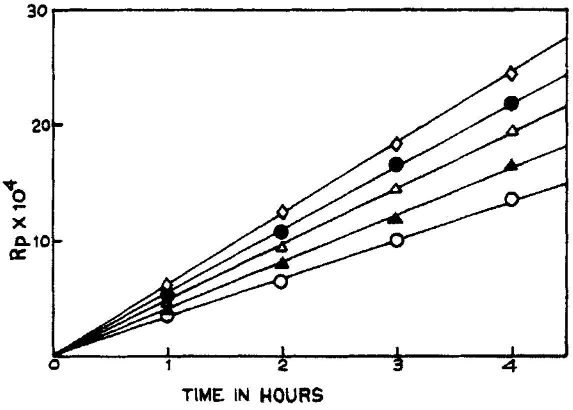

FIG. 9. Effect of inhibitor (picryl chloride) on the rate of polymerization: acid concentration = 1.085 mol/L; monomer concentration = 15.0×10^{-1} mol/L; initiator concentration = 17.48×10^{-3} mol/L; dioxane concentration = 5.85×10^{-1} mol/L; temperature = 70°C. (◇): [picryl chloride] = 0.2×10^{-3} 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.

surfactants. The hydrophobic interactions and the electrostatic attractions are chiefly responsible for the spectacular rate enhancements or inhibitions exhibited by micelles formed from these surfactants [23-25]. Anionic micelles of sodium lauryl sulfate (NaLS) increased the rate and cationic micelles of cetyl trimethyl ammonium bromide (CTABr) decreased the rate (Figs. 10 and 11).

Molecular Weight

Molecular weights of purified polyacrylonitrile were determined by viscometry using the suitable Mark-Houwink-type equation. It was observed that the molecular weight of the polymer increased with an increase in the monomer concentration and decreased with an increase of the dioxane concentration. The chain transfer constant was evaluated by making use of

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

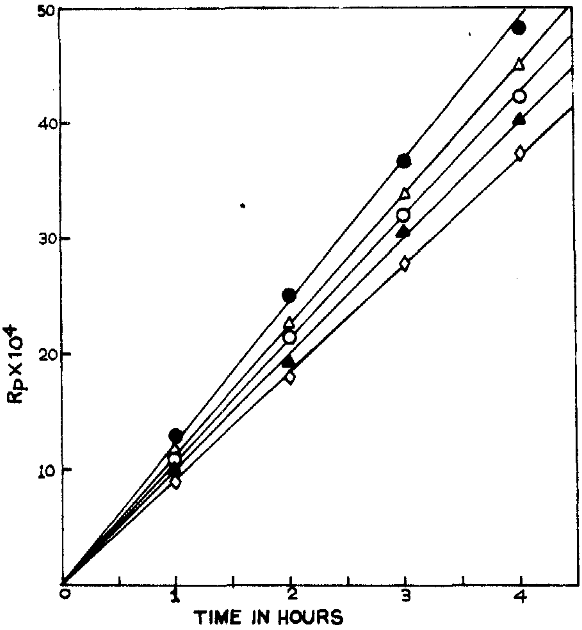

FIG. 10. Effect of anionic surfactant (NaLS) on the rate of polymerization: acid concentration = 1.085 mol/L; monomer concentration = 15.0 × 10^{-1} mol/L; initiator concentration = 17.48 × 10^{-3} mol/L; dioxane concentration = 5.85 × 10^{-1} mol/L; temperature = 70°C. (●): [NaLS] = 8.1 × 10^{-3} mol/L. (△): [NaLS] = 10.0 × 10^{-3} mol/L. (○): [NaLS] = 6.3 × 10^{-3} mol/L. (▲): [NaLS] = 11.25 × 10^{-3} mol/L. (◇): [NaLS] = 5.0 × 10^{-3} mol/L.

where

$$\overline{P}_n = \text{degree of polymerization} = \frac{\text{molecular weight of the polymer}}{\text{molecular weight of the monomer}}$$

$[S]$ = concentration of the solvent (dioxane)

$[M]$ = concentration of the monomer

C_x = chain transfer constant

$\left[1/\overline{P}_n\right]_0$ = constant

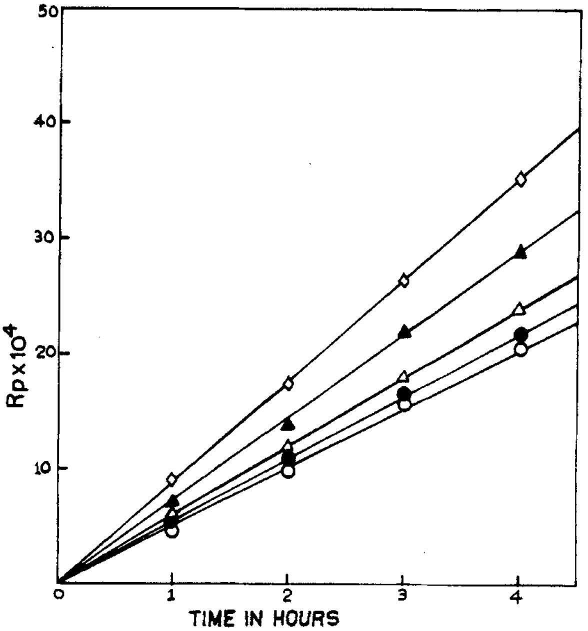

FIG. 11. Effect of cationic surfactant (CTABr) on the rate of polymerization: acid concentration = 1.085 mol/L; monomer concentration = 15.0 × 10^{-1} mol/L; initiator concentration = 17.48 × 10^{-3} mol/L; dioxane concentration = 5.85 × 10^{-1} mol/L; temperature = 70°C, (◇): [CTABr] = 0.7 × 10^{-3} 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.

Plots of $1/\bar{P}_n$ against [S]/[M] give striaght lines (Figs. 12 and 13), their slopes directly giving the value of the chain transfer constants. The chain transfer constant for the monomer (C_M) was calculated to be 1.7 × 10^4 and that for the solvent dioxane (C_S) was 1.6 × 10^4.

MECHANISM

The following mechanism has been suggested for the vinyl polymerization of acrylonitrile initiated by thallium(III) perchlorate in aqueous perchloric acid medium.

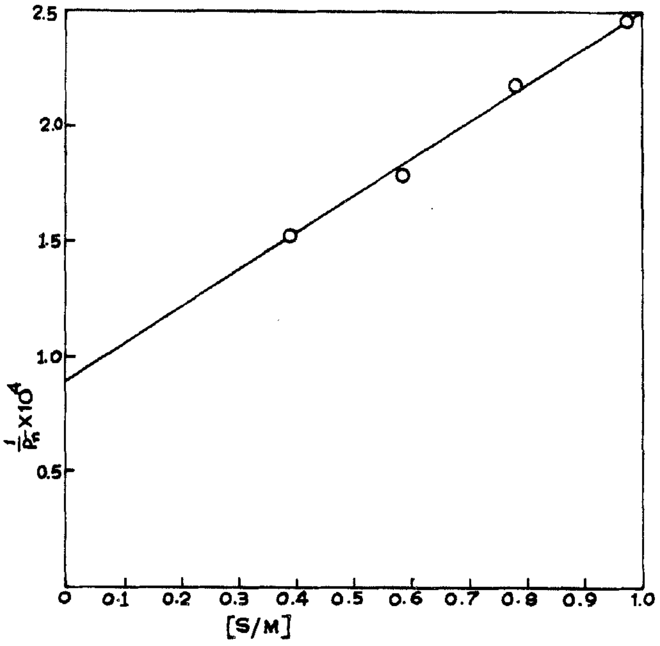

FIG. 12. Variation of molecular weight with dioxane concentration.

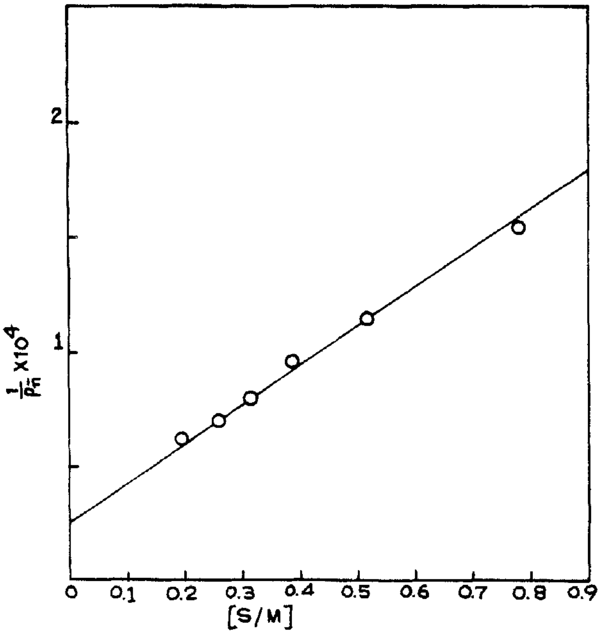

FIG. 13. Variation of molecular weight with monomer concentration.

(i) Production of free radical:

$$Tl(ClO_4)_3 \xrightarrow{k_d} Tl(ClO_4)_2 + ClO_4^{\bullet}$$

(ii) Initiation:

$$ClO_4^{\bullet} + M \xrightarrow{k_i} M^{\bullet}$$

where M is the monomer.

(iii) Propagation:

$$M^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet}$$

$$\vdots$$

$$M_{n-1}^{\bullet} + M \xrightarrow{k_p} M_n^{\bullet}$$

(iv) Termination:

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

Taking into account the mutual termination and assuming steady state for the free radicals, the rate laws have been derived as follows:

$$-\frac{d[ClO_4^{\bullet}]}{dt} = k_d[I] - k_i[ClO_4^{\bullet}][M] = 0$$

where [I] is the concentration of thallium(III) perchlorate.

Thus

$$[ClO_4^{\bullet}] = \frac{k_d[I]}{k_i[M]}$$

$$-\frac{d[M_n^{\bullet}]}{dt} = k_i[M][ClO_4^{\bullet}] - k_t[M_n^{\bullet}]^2 = 0$$

or

$$[M_n^{\cdot}] = \left\{ \frac{k_i[M][ClO_4^{\cdot}]}{k_t} \right\}^{1/2}$$

Substituting the value of $[ClO_4^{\cdot}]$ in the above equation,

$$[M_n^{\cdot}] = \left\{ \frac{k_d[I]}{k_t} \right\}^{1/2}$$

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

or

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

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

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