

The Cupric Sulfate-Hydrazine-Oxygen System as an Initiator for the Emulsion Polymerization of Methyl Methacrylate

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INTRODUCTION

The use of the cupric sulfate-hydrazine system as an initiator for the aqueous solution polymerization of methyl methacrylate has been reported in a preliminary study by Menon and Kapur.¹ These workers postulate that the hydrazyl radical, which is reported²⁻⁴ as an intermediate in the catalytic decomposition of hydrazine, is responsible for the initiation of the polymerization.

The present authors have investigated the detailed kinetics of polymerizations utilizing this initiator and also the influence of heterogeneous phases (e.g., precipitating polymer and catalyst surface) on the mechanism of the polymerizations.⁵⁻⁸ These authors showed that hydrazine decomposes both in solution when the decomposition is catalyzed by cupric ions, and also on the cupric hydroxide sol, and precipitate which are present at cupric sulfate concentrations greater than 5×10^{-5} mole liter⁻¹ and 10^{-4} mole liter⁻¹, respectively.

The present work is an examination of the kinetics of the emulsion polymerization of methyl methacrylate initiated by the cupric sulfate-hydrazine system in the presence of oxygen.

EXPERIMENTAL

Preparation and Purification of Materials

Methyl Methacrylate. Stabilized methyl methacrylate was distilled under reduced pressure in an atmosphere of nitrogen and used immediately.

Hydrazine Hydrate. The concentration of each freshly prepared solution of hydrazine hydrate was estimated by titrating 5 ml of the solution with 0.25*N* potassium iodate solution in the presence of 5 ml 12*N* hydrochloric acid and 2 ml chloroform. The solution was used immediately.

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Cupric Sulfate. Analytical reagent grade cupric sulfate was used and on analysis was found to be 99.5% pure, containing less than 0.02% ferric ion.

Sodium Dodecyl Sulfate. Sodium dodecyl sulfate obtained from Sigma Chemical Co., Ltd. and specified as 99.9% pure was used throughout this investigation.

Method

The apparatus consisted of a 250 ml, three-necked, round-bottom flask. This was fitted with an oxygen inlet, condenser, stirrer, and narrow bore tap through which samples of the reaction mixture were extracted. The apparatus was immersed in a constant temperature bath.

The standard reaction mixture is:

- 22.5 g methyl methacrylate (distilled)
- 23.0 ml 0.16 mole liter⁻¹ sodium dodecyl sulfate solution
- 8.4 ml 10⁻³ mole liter⁻¹ cupric sulfate solution
- 6.0 ml 2.0 mole liter⁻¹ hydrazine hydrate solution
- 90.1 ml deionized water

The total water phase was held constant for each experiment.

The pH of the resultant mixture was 10.0. At this pH cupric hydroxide is formed.⁵

The solutions of cupric sulfate and sodium dodecyl sulfate were added to the water in the flask. Oxygen was passed through the stirred solution for one hour, after which time the methyl methacrylate was added. The flow of oxygen was then reduced to a rate which did not result in any undue loss of monomer by evaporation. This rate was then maintained for the duration of the experiment. The mixture was then stirred as vigorously as possible for 15 min, so as to homogenize the system. The stirring rate was then reduced to about seven revolutions per second which adequately maintained the dispersion of monomer in the aqueous phase.

Polymerization was started by the addition of the hydrazine hydrate solution through the tap on the flask, the solution being added from a hypodermic syringe. Samples were withdrawn at intervals of time during the course of the reaction and, after weighing and quenching with a solution of hydroquinone in acetone, these were dried in an oven at 70°C.

The percentage conversion represented by a particular sample was calculated from the formula:

$$\% \text{ conversion} = \frac{RT}{S} - N$$

R = weight of residue, T = total weight of all ingredients (based on 100 parts monomer), S = weight of sample taken, N = number of parts of involatile solids.

Five milliliter samples of latex were also withdrawn for analysis for hydrazine content. This was done by titrating the samples with 0.25*N*

potassium iodate solution in the presence of 5 ml 12*N* hydrochloric acid and 5 ml chloroform and 10 ml water. The end point was at first difficult to discern, due to its being somewhat masked by the precipitated soap, but with practice, this error was minimized and consistent results obtained. The rate of hydrazine decomposition was taken at a time equivalent to a point half-way through the zero order rate of polymerization.

Results

The curves of "percentage conversion" vs. "time" were of the same form as those obtained by Zimmt,⁹ a pronounced Trommsdorff effect being observed in some cases. In these latter cases it was sometimes difficult to decide which was the true zero order rate. The extreme cases illustrated by Zimmt, for particles above 0.38 microns diameter, were not observed during the course of this study.

Figure 1 shows the variation of polymerization rate and Figure 2 the variation of hydrazine decomposition rate with change in cupric sulfate concentration. No emulsion polymerization occurs below a cupric sulfate

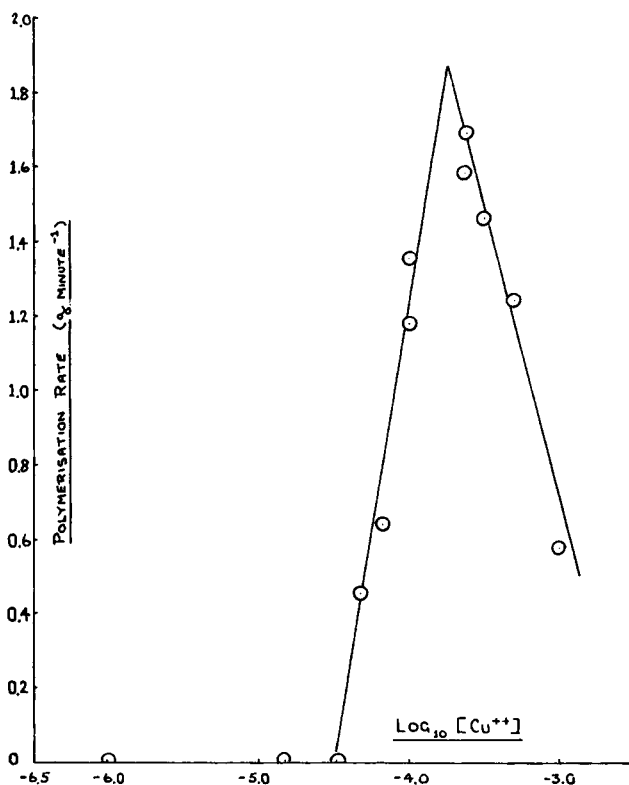


Fig. 1. The dependence of the zero order rate of polymerization on the concentration of cupric sulfate. (0.08 mole liter⁻¹ hydrazine hydrate, 0.03 mole liter⁻¹ sodium dodecyl sulfate, 15% methyl methacrylate, temperature—30°C.)

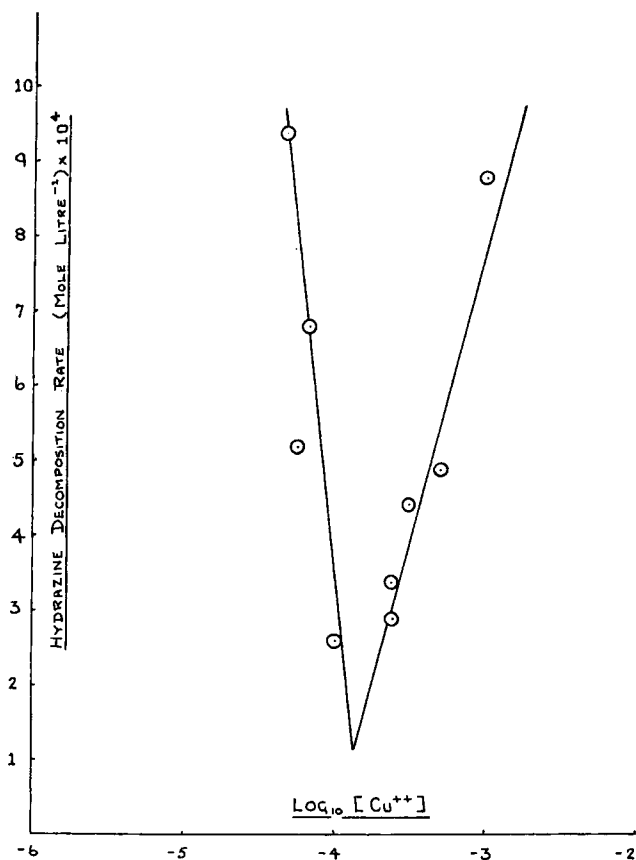


Fig. 2. The dependence of the rate of decomposition of hydrazine on the concentration of cupric sulfate. (0.08 mole liter⁻¹ hydrazine hydrate, 0.03 mole liter⁻¹ sodium dodecyl sulfate, 15% methyl methacrylate, temperature—30°C.)

concentration of 3.4×10^{-5} moles liter⁻¹. Above this concentration the rate of polymerization is proportional to the cupric sulfate concentration, reaching a maximum at 1.8×10^{-4} mole liter⁻¹ cupric sulfate and falling off at higher concentrations.

The rate of decomposition of hydrazine decreases to a minimum at 1×10^{-4} mole liter⁻¹ cupric sulfate. At cupric sulfate concentrations greater than this the rate increases with increasing cupric sulfate concentration.

The dependence of the rate of polymerization on hydrazine concentration is shown in Figure 3. No emulsion polymerization takes place at concentrations of hydrazine less than 0.04 mole liter⁻¹. At concentrations of hydrazine greater than this, the rate is proportional to the initial hydrazine concentration reaching a maximum at 0.08 mole liter⁻¹ hydrazine. Any further increase in the hydrazine concentration does not affect the polymerization rate.

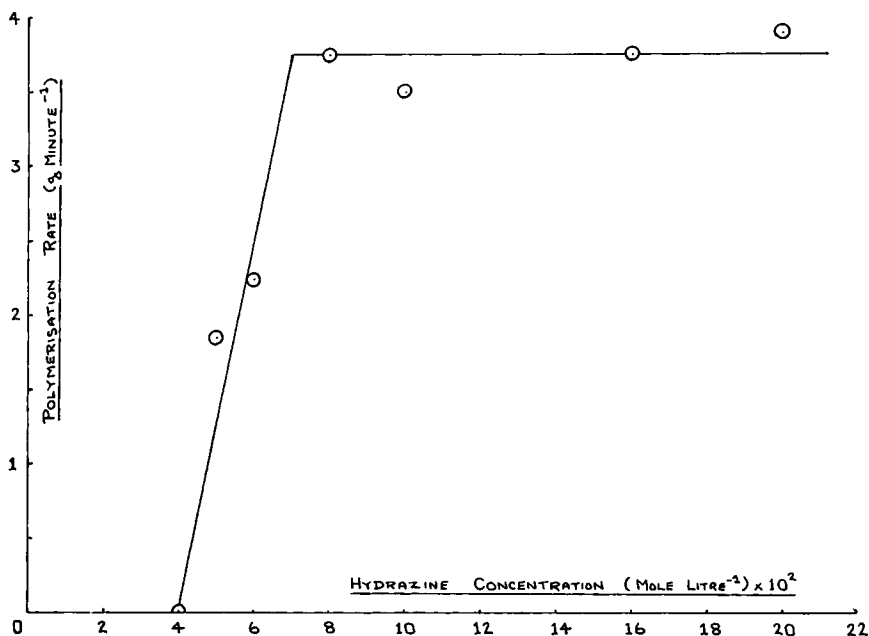


Fig. 3. The dependence of the zero order rate of polymerization on the concentration of hydrazine hydrate. (6.6×10^{-5} mole liter⁻¹ cupric sulfate, 0.03 mole liter⁻¹ sodium dodecyl sulfate, 15% methyl methacrylate, temperature—30°C.)

The ratio of monomer concentration to soap concentration was varied in such a way as to maintain a constant number of micelles in the aqueous phase. Figure 4a shows that the zero order rate of polymerization is independent of monomer concentration up to a ratio of 15.5 g monomer/g soap. Above this concentration the rate of polymerization is proportional to the ratio of monomer concentration to soap concentration. The rate of hydrazine decomposition is also proportional to the ratio of monomer concentration to soap concentration (Fig. 4a).

Figure 5 shows that the rate of polymerization is dependent on the soap concentration. This will be discussed later.

The dependence of the rate of hydrazine decomposition on the soap concentration is unusual in that the rate decreases with increasing soap concentration reaching a minimum at 0.06 mole liter⁻¹ and thereafter increasing with increasing soap concentration (Fig. 6). The critical micelle concentration of sodium dodecyl sulfate is reported as 0.008 mole liter⁻¹.¹⁰

Figure 7 shows the dependence of the rate of polymerization and Figure 8 the dependence of the rate of hydrazine decomposition on temperature. The zero order rate of polymerization increases with increasing reaction temperature. Above 40°C the increase is only slight with any further increase in temperature. The same effect was observed for the emulsion polymerization of *n*-butyl methacrylate, the change in gradient taking

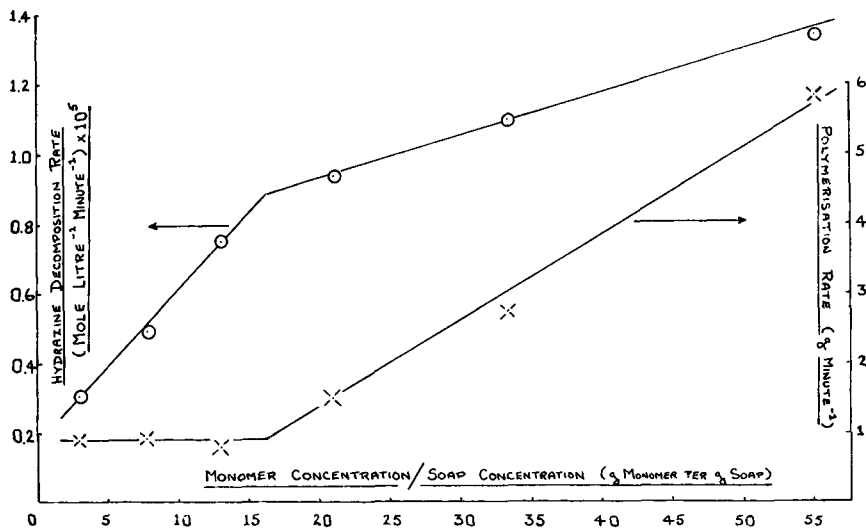


Fig. 4a. Reaction at 30°C, $6.6. \times 10^{-5}$ mole liter⁻¹ cupric sulfate, 0.08 mole liter⁻¹ hydrazine hydrate, 0.03 mole liter⁻¹ sodium dodecyl sulfate. *a*, The dependence of the rate of hydrazine decomposition on the ratio of monomer concentration to soap concentration. *b*, The dependence of the zero order rate of polymerization on the ratio of monomer concentration to soap concentration.

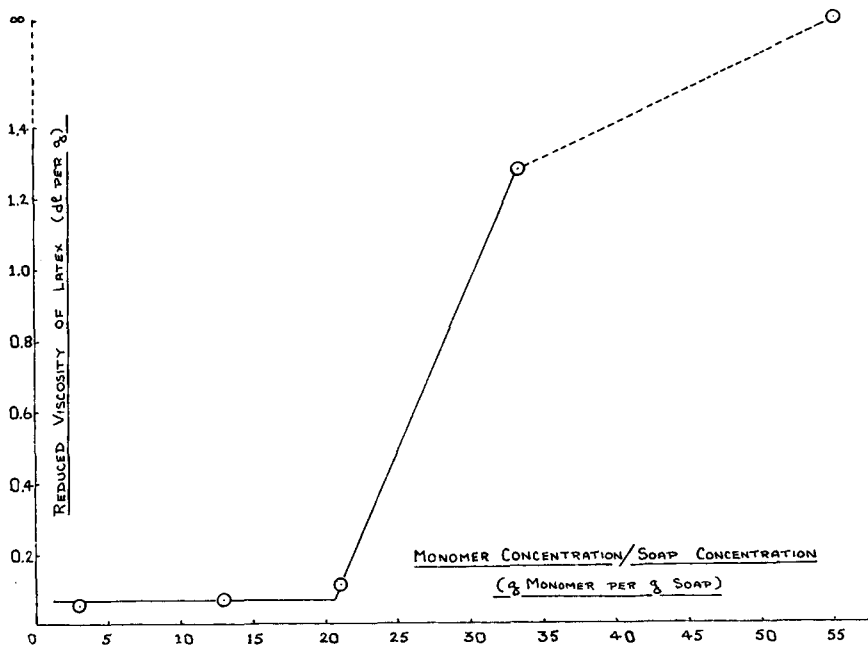


Fig. 4b. The dependence of the reduced viscosity on the ratio of monomer concentration to soap concentration.

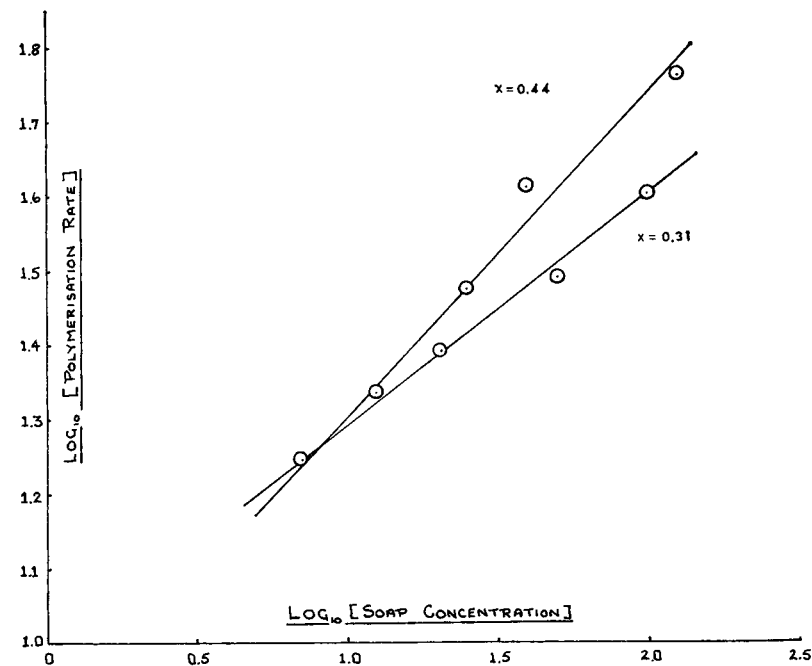


Fig. 5. The zero order rate of polymerization as a function of soap concentration. (6.6×10^{-5} mole liter⁻¹ cupric sulfate, 0.08 mole liter⁻¹ hydrazine hydrate, 15% methyl methacrylate, temperature—30°C.)

place at about 37°C. This rules out the effect being due to the water solubility of methyl methacrylate since *n*-butyl methacrylate is virtually insoluble in water.

An Arrhenius plot for the methyl methacrylate polymerization yields an activation energy for the complete process of 23.7 kcal mole⁻¹ for a concentration of 0.46% sodium dodecyl sulfate. This is in fair agreement with the work of Kanamaru et al.¹¹ who found an activation energy of 24.4 kcal mole⁻¹ for the "emulsion" polymerization of methyl methacrylate in the absence of emulsifier and an activation energy of 16.6 kcal mole⁻¹ in the presence of 1% sodium dodecyl sulfate.

The rate of hydrazine decomposition increases linearly with increasing temperature over the range 30–50°C, the rate quadrupling. The activation energy for this decomposition was found to be 3.4 kcal mole⁻¹, the rate being taken at one third decomposition.

DISCUSSION

The dependence of the rate of the emulsion polymerization of methyl methacrylate on cupric sulfate concentration is of the same form as that for the solution polymerization.⁵ The only difference is that the maximum rate of emulsion polymerization occurs at a cupric sulfate concentration of

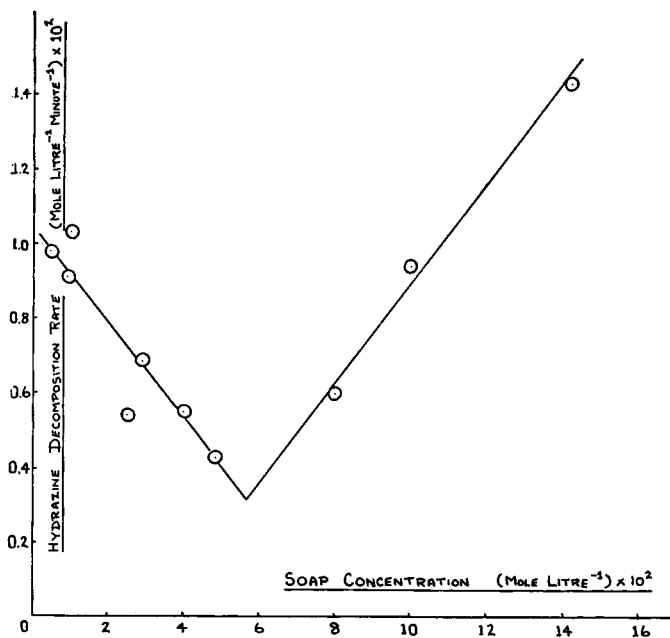


Fig. 6. The dependence of the rate of decomposition of hydrazine on soap concentration. (6.6×10^{-5} mole liter⁻¹ cupric sulfate, 0.08 mole liter⁻¹ hydrazine hydrate, 15% methyl methacrylate, temperature— 30°C .)

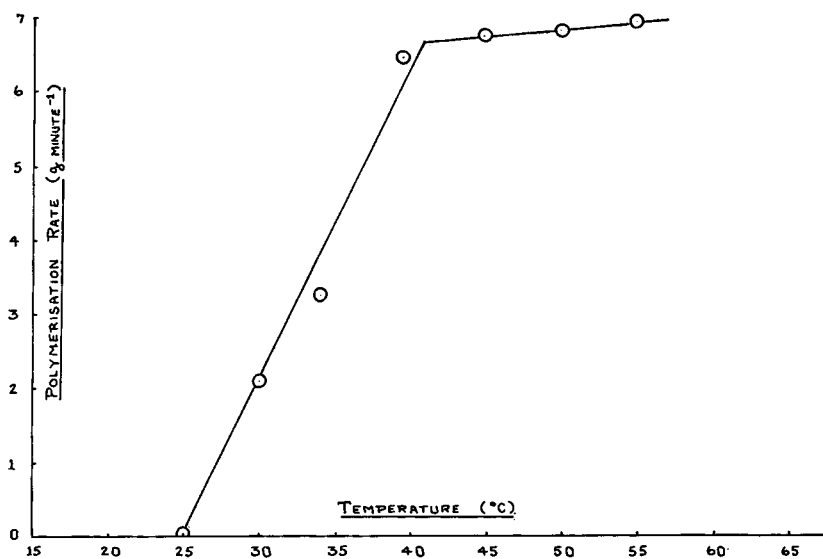


Fig. 7. The dependence of the zero order rate of polymerization on temperature. (6.6×10^{-5} mole liter⁻¹ cupric sulfate, 0.08 mole liter⁻¹ hydrazine hydrate, 0.03 mole liter⁻¹ sodium dodecyl sulfate, 15% methyl methacrylate.)

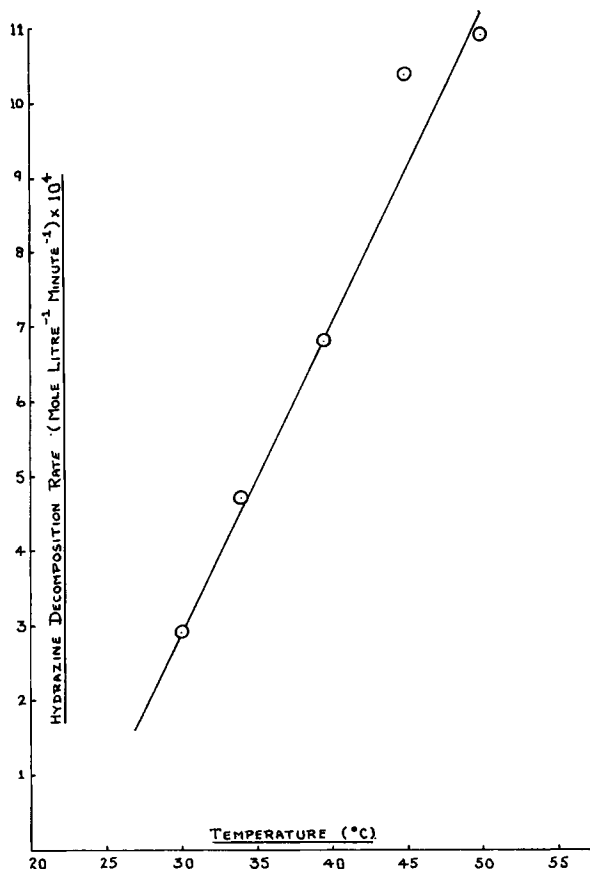


Fig. 8. The dependence of the rate of decomposition of hydrazine on temperature. (6.6×10^{-5} mole liter⁻¹ cupric sulfate, 0.08 mole liter⁻¹ hydrazine hydrate, 0.03 mole liter⁻¹ sodium dodecyl sulfate, 15% methyl methacrylate.)

1.8×10^{-4} mole liter⁻¹, whereas that for solution polymerization occurs at a concentration of 10^{-5} mole liter⁻¹ cupric sulfate; also, at this latter concentration no emulsion polymerization takes place.

Kolthoff and Johnson¹² have shown that ions can be adsorbed by micelles out of bulk solution, so as to form counter-ions for the micelles. This adsorption results in an increase in the apparent solubility of the adsorbed ion. Thus it would seem that below a cupric sulfate concentration of 3.4×10^{-5} mole liter⁻¹ most of the cupric sulfate is adsorbed on the micelles and too few initiating free radicals, which result from the decomposition of the hydrazine catalyzed by this type of cupric ion, are available for the initiation of emulsion polymerization. Polymer is however produced as a result of solution polymerization which shows that there is competition between dissolved monomer molecules and micelles for the primary radicals. This also indicates that the emulsion polymerization of methyl methacrylate is

initiated by the primary radicals and not by "oligomer-radicals" which is proposed by van der Hoff¹³ for the persulfate initiated emulsion polymerization of styrene. The same effect is observed for the dependence of polymerization rate on hydrazine concentration which is discussed later.

It would seem anomalous that the rate of polymerization increases as the rate of decomposition of hydrazine decreases. Over this concentration range of cupric sulfate two effects are taking place (1) cupric hydroxide, which is in the form of a sol at about 5×10^{-5} mole liter⁻¹, starts to precipitate at about 10^{-4} mole liter⁻¹.⁵ (2) the number of micelles increases with increasing cupric sulfate concentration. This latter effect of ionic strength is well known.¹⁴ Thus, even though the rate of hydrazine decomposition is decreasing, the increase in the number of micelles compensates for this, and the rate of polymerization increases. Even at the minimum rate of hydrazine decomposition, 48×10^{-20} radicals liter⁻¹ minute⁻¹ are produced, and this number adequately meets the number of radicals required by the Smith-Ewart mechanism.²³

The decrease in the rate of hydrazine decomposition is thought to be the result of two effects.

(1) The adsorption of cupric ions on the micelles. As the cupric sulfate concentration is increased, the number of micelles increases because of the increase in ionic strength. This means that there are more micelles available for the adsorption of cupric ions (as previously described) and some of the cupric hydroxide sol should redissolve in order to restore the equilibrium. The layer of adsorbed soap on the surface (discussed below) hinders this dissolution. Thus, at concentrations above the saturation solubility of cupric hydroxide, increasing the cupric sulfate concentration decreases the effective concentration of cupric ions in true solution.

(2) The adsorption of soap on the cupric hydroxide surface. This effect has been shown to take place by studying the rate of hydrazine decomposition in the presence and absence of sodium dodecyl sulfate. In the presence of the soap the rate is half that in its absence. These rates are given below.

(a) hydrazine + 10^{-4} mole liter⁻¹ cupric sulfate — 24×10^{-4} g min⁻¹

(b) hydrazine + 10^{-4} mole liter⁻¹ cupric sulfate + sodium dodecyl sulfate — 12×10^{-4} g min⁻¹

The decrease in rate of polymerization along with the increase in the rate of hydrazine decomposition at cupric sulfate concentrations where precipitation of cupric hydroxide occurs was explained for the solution polymerization⁵ to be the result of adsorption and mutual annihilation of primary radicals on the surface of the precipitate—a well known effect in chain reactions.¹⁵

The effect of the hydrazine concentration on the rate of emulsion polymerization is again similar to that found in the solution polymerization. In the latter case the zero order dependency started at 0.005 mole liter⁻¹ hydrazine. The curve has been displaced by a fast reaction which takes

place between methyl methacrylate and hydrazine, and this will be discussed later. As a result of this reaction a minimum concentration of 0.04 mole liter⁻¹ hydrazine is required before a sufficient number of free radicals is available to initiate emulsion polymerization—solution polymerization was observed below 0.04 mole liter⁻¹ hydrazine. When the concentration of free radicals is sufficient, so that any further increase in free radical concentration does not result in more micelles being stung (mutual annihilation becoming important), then the rate of polymerization will become independent of hydrazine concentration, as was observed.

The fact that the rate of hydrazine decomposition increases with increasing monomer to soap ratio (Fig. 4a) indicates that a reaction is taking place between methyl methacrylate and hydrazine. When an aqueous solution of hydrazine was stirred with methyl methacrylate in the absence of oxygen, a white solid precipitated (at 30°C); this solid was found to be surface active when in aqueous solution. The hydrazine was consumed at a rate of 6.25×10^{-4} g min⁻¹ whereas with no methyl methacrylate present no decomposition of hydrazine could be detected. A patent to Olin Industries Inc.¹⁶ describes the use of compounds, formed by the addition of hydrazine to fatty acids, as emulsifiers for oil in water emulsions.

The formation of a surface active agent explains the observed deviation from the usual zero order dependency of the rate of polymerization on monomer concentration (Fig. 4a). The observation of a critical ratio merely indicates that a sufficient excess of methyl methacrylate is required over that consumed by the faster polymerization reaction for enough surface active agent to be produced in order to enable more particles to be formed.

The increase in the rate of hydrazine decomposition with increasing ratio of monomer concentration to soap concentration is less above a ratio of 15.5 than below it. This shows that above this ratio the increase in the number of particles, due to the formation of surface active agent, is sufficient to allow the polymerization reaction to become predominant. The methyl methacrylate is then preferentially consumed by the polymerization rather than by its reaction with hydrazine.

An electron microscopic study was undertaken to prove the increase in particle number at ratios of monomer concentration to soap concentration greater than 15.5. This was, however, found to be impossible because of the extreme sensitivity of the polymer to the electron beam—the particles de-polymerized. When the viscosity average molecular weights were determined it was found that they varied from $\sim 10^3$ to $\sim 10^5$ which is low and would account for the high beam sensitivity. The molecular weights of the polymer studied by Brodnyan et al.¹⁸ were $\sim 10^7$.

It was decided that the very large increase in particle number which the kinetics predict (Fig. 4a) should increase the viscosity of the latex to such a degree as to outweigh any error due to alteration in particle size distribution. (This latter is found to affect latex viscosity.²²) Figure 4b shows that the viscosity of the latex does indeed follow the expected trend, i.e., it is

virtually constant up to a ratio of monomer concentration to soap concentration of 21, after which it rises steeply to infinity.

Gershberg¹⁷ has shown that monomers which have a water solubility greater than 0.04–0.07% deviate considerably from Smith–Ewart kinetics.²³ He proposes an empirical expression:

$$R_p \propto (S)^{x \pm 0.07} (C_0)^{0.45 \pm 0.05} (P)^0$$

where

- R_p = polymerization rate
- S = emulsifier concentration
- C_0 = initial catalyst concentration
- P = phase ratio

x varies with changing water solubility and for monomers whose water solubility is less than 0.04–0.07%, x equals 0.6 as predicted by the Smith–Ewart theory. For methyl methacrylate Gershberg quotes x equal to 0.3–0.4.

Figure 5 shows that in the present study x equals 0.31–0.44. A comparison of the plot of R_p vs. $[\text{Soap}]^{0.31}$ with the plot of R_p vs. $[\text{Soap}]^{0.6}$ showed that both plots are linear but that the plot of $[\text{Soap}]^{0.31}$ has considerably less scatter than the plot of $[\text{Soap}]^{0.6}$. It would seem that considerable care is required when the Smith–Ewart mechanism is interpreted in the light of kinetic data. This agrees with the findings of Brodnyan et al.¹⁸ that kinetic data alone cannot confirm the Smith–Ewart theory. Contrary to Gershberg, Brodnyan concluded that the water solubility of the monomer is relatively unimportant in determining the rate dependence on soap concentration and they found that for both methyl and *n*-butyl methacrylates $R_p \propto (S)^{0.5}(C_0)^{0.5}$. Zimmt⁹ concluded from a particle size study that methyl methacrylate follows the Smith–Ewart theory.

Figure 6 further illustrates the effects that the presence of emulsifying agents can have on metal catalyzed initiators. The decrease in the rate of hydrazine decomposition with increasing soap concentration is accounted for in the same manner as the decrease in rate of hydrazine decomposition with increasing cupric sulfate concentration, i.e., adsorption of soap on the cupric hydroxide surface.

The increase in the rate of hydrazine decomposition with increasing soap concentration (at soap concentrations greater than 0.06 mole liter⁻¹) is explained by the preferential adsorption of soap on monomer-swollen polymer particles. At a constant monomer concentration an increase in soap concentration results in an increase in total particle surface area. Thus, when the total surface area of polymer particles is large enough to require all the soap present for stabilizing the particles, and if the soap is preferentially adsorbed on the particles, then soap will desorb from the cupric hydroxide and adsorb on the polymer particles. The following rates for the decomposition of hydrazine confirm that this mechanism is likely.

- (a) 0.08 mole liter⁻¹ hydrazine +
0.03 mole liter⁻¹ sodium
dodecyl sulfate +
 6.6×10^{-5} mole liter⁻¹ CuSO₄ 2.5×10^{-3} g min⁻¹
- (b) 0.08 mole liter⁻¹ hydrazine +
0.03 mole liter⁻¹ sodium
dodecyl sulfate +
 6.6×10^{-5} mole liter⁻¹ CuSO₄
+ poly(methyl methacrylate)
equiv. to 50% conversion 7.5×10^{-3} g min⁻¹
- (c) 0.08 mole liter⁻¹ hydrazine +
0.03 mole liter⁻¹ sodium
dodecyl sulfate +
 6.6×10^{-5} mole liter⁻¹ CuSO₄
+ poly(methyl methacrylate)
equiv. to 50% conversion +
benzene (1.5 g/g polymer)¹⁹ 11.3×10^{-3} g min⁻¹

The increase in the rate of hydrazine decomposition from 3.5 to 7.5 g min⁻¹, when poly(methyl methacrylate) is present in the reaction mixture, illustrates the preferential adsorption of sodium-dodecyl sulfate on the polymer. The strong adsorption on monomer-swollen polymer is illustrated by the increase in rate from 7.5 to 11.3 g min⁻¹ when benzene-swollen polymer is used.

Bond and Jones²⁰ have shown that in the case of the hydrogen peroxide initiated emulsion polymerization of styrene it is necessary to add the peroxide over a period of time, so that the localized concentration of free radicals is too small for mutual annihilation to take place to any significant degree. If all the peroxide is added at the start of the reaction low yields of polymer are obtained. This effect has been shown to occur for the emulsion polymerization of methyl methacrylate initiated by the manganic-hydrazine system.²¹

Figure 7 shows that above 40°C the rate of polymerization is nearly independent of temperature in spite of the fact that the rate of hydrazine decomposition increases with increase in temperature over the whole range. It thus seems likely that, at the high free radical fluxes which would be encountered at the higher temperatures, mutual annihilation becomes important thus effectively maintaining a constant rate of diffusion of free radicals into the particles with increasing temperature (above 40°C).

CONCLUSIONS

The cupric sulfate hydrazine system in the presence of oxygen is a good initiator for the emulsion polymerization of methyl methacrylate.

The kinetics appear to follow the scheme propounded by Gershberg rather than the traditional Smith-Ewart mechanism.

There are indications that the initiation of the emulsion polymerization takes place in the micelle rather than in the aqueous phase and that solution polymerization is a competing rather than a complementary reaction. Another important side reaction is that between methyl methacrylate and hydrazine. This results in no polymerization taking place at low-hydrazine concentrations and an unusually high rate of polymerization at high monomer concentrations owing to the formation of a surface active product.

Sodium dodecyl sulfate has a profound effect on this redox initiator in that cupric ions are adsorbed on micelles and the soap is also adsorbed on the surface of the cupric hydroxide catalyst, thereby causing a reduction in the rate of hydrazine decomposition.

SUMMARY

The kinetics of the emulsion polymerization of methyl methacrylate initiated by the cupric sulfate-hydrazine system in the presence of oxygen have been evaluated.

A maximum rate of polymerization occurs at a cupric sulfate concentration of 1.8×10^{-4} mole liter⁻¹. The adsorption of cupric ion on the micelles and the adsorption of soap on cupric hydroxide are discussed as an explanation of this effect.

A reaction between hydrazine and methyl methacrylate produces a surface active agent which enhances the rate of polymerization and increases the number of particles at high ratios of monomer concentration to soap concentration.

The kinetics follow the mechanism of Gershberg rather than that of Smith and Ewart, and the initiation of the emulsion polymerization appears to take place inside the micelle rather than in the aqueous phase as was proposed by van der Hoff for styrene.

The activation energy for the complete process is 23.7 kcal mole⁻¹.

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