# The Ferric Hydroxide/Hydrazine System as an Initiator of Vinyl Polymerization

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## Synopsis

The reaction between ferric hydroxide and hydrazine was used to initiate the solution polymerization of methyl methacrylate. Polymerization occurs readily at pH > 6, over a wide range of iron concentration and of temperature. The initiation reaction appears to be of heterogeneous nature, like those in similar metal hydroxide/hydrazine systems.

## INTRODUCTION

Recent reports[1-6] have described the use of the reactions between both Cu(II) and Mn(III) hydroxides and hydrazine as initiators of vinyl polymerization, in both solution and emulsion systems. The pronounced similarity in behavior of these two systems prompted the investigation of another system in which the insoluble hydroxide of the higher valency state of a metal is coupled with hydrazine. The present communication reports the application of the ferric hydroxide/hydrazine system to the solution polymerization of methyl methacrylate.

## 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.** A fresh aqueous solution was prepared for each experiment, using hydrazine hydrate of at least 98% purity as stock solution.

**Ammonium Ferric Sulfate.** Analytical reagent-grade ammonium ferric sulfate was used, at least 99.5% pure and containing not more than 0.02% copper and 0.01% manganese.

## Polymerization

The method used was based upon that employed by Bond and Lee.[2] The apparatus consisted of 12 tubes immersed in a constant-temperature water bath. Each tube was fitted with a gas inlet tube and a condenser. Oxygen was supplied to all the tubes from the same cylinder by means of a 12-piece manifold.

The general reaction mixture was: "x" ml, 0.125 mole/l. methyl methacrylate solution; "y" ml, 1.0 mole/l. hydrazine hydrate solution; "z" ml of standard ferric ammonium sulfate solution containing 0.12 mole/l. hydrochloric acid to prevent precipitation of ferric hydroxide; 5-"z" ml 0.12 mole/l. hydrochloric acid; and 50-("x" + "y" + 5) ml deionized water. The pH of the final mixture was 9.0 ± 0.1.

The water, ferric ammonium sulfate solution, and hydrochloric acid solution were added to each tube and the mixtures were saturated with oxygen by passing a stream of the gas through for 1 hr. After this time the flow rate was reduced to 2 bubbles per second and the monomer solution was added, followed by the hydrazine solution. The two latter solutions were prepared using oxygen-saturated water. At this point the flow of oxygen was terminated to prevent the occurrence of long induction periods.

The polymerization in a particular tube was stopped after the chosen period of time by addition of 5 ml hydrochloric acid solution (4.0 mole/l.). In this way, the amounts of polymer formed after various intervals of time are obtained, and it is possible to construct a rate curve from many separate experiments, provided that reproducible induction periods are obtained.

After the addition of the hydrochloric acid, the tube was allowed to stand for 1 hr for complete coagulation to occur. The suspension was then filtered through a preweighed sintered glass crucible which was then dried to constant weight in an oven at 70°C. The crucibles were cooled in a desiccator over silica gel. The per cent conversion was calculated in each case and plotted against time. The reaction rate was calculated from the straight line obtained.

The filtrates were examined for residual hydrazine, e.g., 5-ml aliquots were titrated with potassium iodate solution (0.03125 mole/l.) in the presence of 5 ml of hydrochloric acid (12 mole/l.) and 2 ml chloroform.

## RESULTS AND DISCUSSION

Satisfactory and reproducible polymerization occurred only when the oxygen bubbling was terminated immediately following the addition of the hydrazine. Continuation of the bubbling beyond this point resulted in irregular induction periods. Attempts at polymerization in the complete absence of oxygen, under an atmosphere of nitrogen, were unsuccessful.

The dependence of rate of polymerization upon ferric hydroxide concentration is shown in Figure 1, which also shows the variation in rate of hydrazine decomposition. The rate of polymerization curve shows a sharp
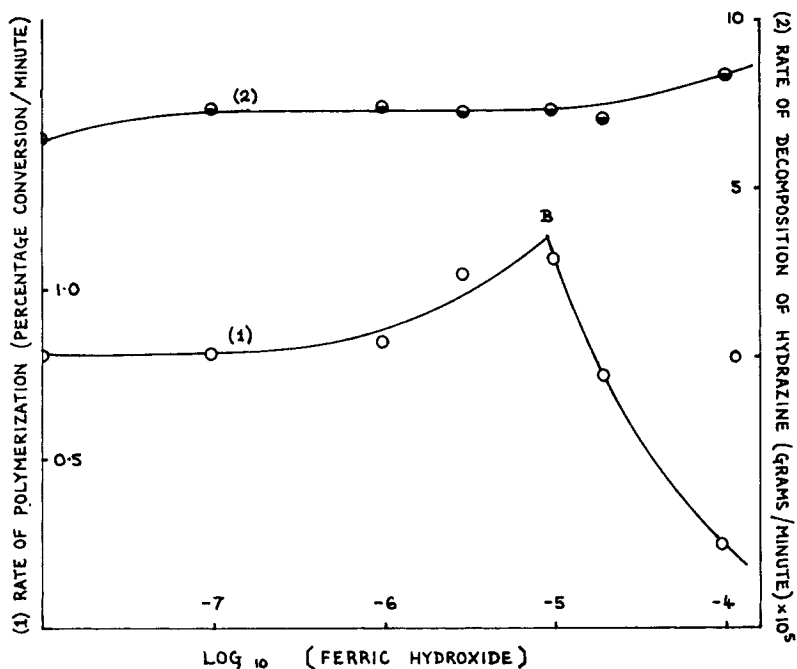
Fig. 1. Dependence of zero-order rate of solution polymerization (1) and rate of hydrazine hydrate decomposition (2) on ferric hydroxide concentration. Hydrazine hydrate, 0.08 mole/l.; methyl methacrylate, 0.02 mole/l.; temperature, 30°C; pH 9.0.

peak at a ferric ion concentration of $1 \times 10^{-5}$ mole/l. (point B), which corresponds to the saturation solubility of ferrous hydroxide. The shapes of these curves can be explained as follows. The rate of polymerization increases with increasing ferric concentration up to point B, and there is a corresponding increase in the rate of hydrazine decomposition. In this region, the hydrazine can react on the surface of the insoluble ferric hydroxide producing initiating radicals and soluble ferrous hydroxide. The latter is converted back into ferric hydroxide by the oxygen present. At ferric concentrations greater than $10^{-5}$ mole/l. (corresponding to point B), insoluble ferrous hydroxide will be present and the rate of polymerization will be lowered as a result of adsorption of primary radicals on its surface and subsequent mutual annihilation. Behavior of a broadly similar type has been observed[2-6] using manganese/hydrazine and copper/hydrazine initiators in both solution and emulsion polymerization of methyl methacrylate, and the same type of explanation has been advanced.

The remaining studies were carried out at a fixed ferric ammonium sulfate concentration of $10^{-6}$ mole/l.

**Variation of pH** (shown in Fig. 2). The rates of polymerization and of hydrazine decomposition show parallel behavior, viz., the reaction rate decreases rapidly as the pH is lowered and becomes undetectable below pH 6. This behavior is attributed to the increasing amount of hydrazine which
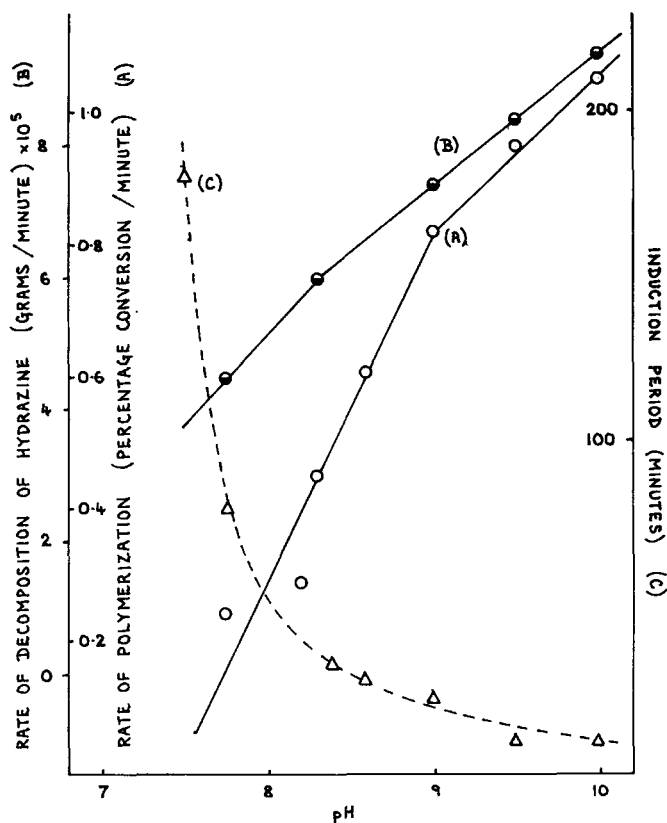
Fig. 2. Dependence of zero-order rate of solution polymerization (A), rate of hydrazine hydrate decomposition (B), and induction period (C) on pH. Ferric ammonium sulfate, $10^{-6}$ mole/l.; hydrazine hydrate, 0.08 mole/l.; methyl methacrylate, 0.02 mole/l.; temperature, 30°C.

is present as hydrazinium ion as the pH is lowered, resulting in a decreased concentration of hydrazine hydrate, which is the active species.

**Variation of Temperature.** The variation of rate of polymerization with temperature is shown in Figure 3. An Arrhenius plot of these results is shown in Figure 4, from which an activation energy of 19.3 kJ/mole can be calculated, a value of the same order as is usually found[7] for similar addition polymerization reactions. The rate of decomposition of hydrazine is virtually independent of temperature, indicating that the surface-catalyzed decomposition of hydrazine has an extremely small activation energy.

**Variation of Initial Hydrazine Concentration.** The effect of this variation on the rate of decomposition of hydrazine is shown in Figure 5. (In these experiments, the extent of decomposition after 60 min was measured rather than the actual reaction rate. This shorter procedure was adopted in some cases after it had been established[8] that the two procedures gave essentially similar results.) It can be seen that the rate of decomposition
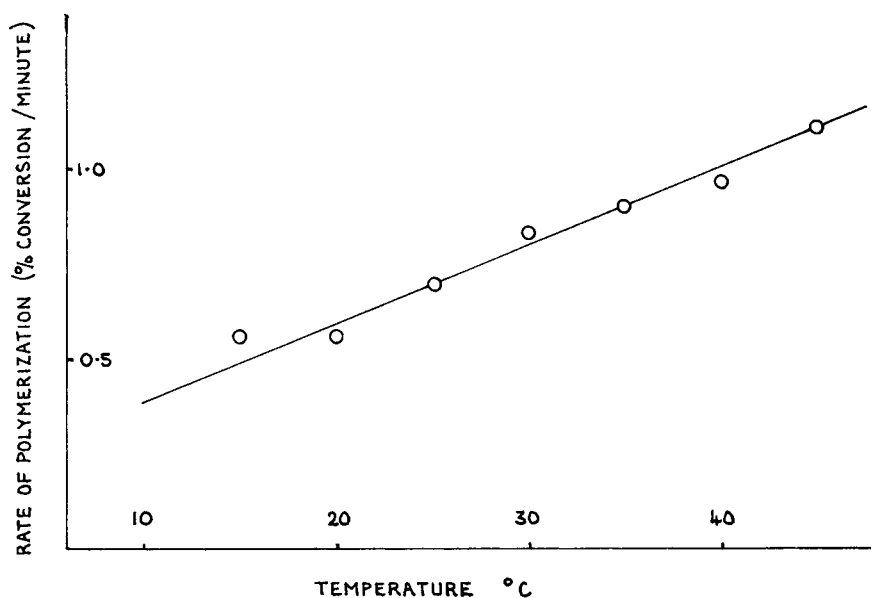
Fig. 3. Dependence of zero-order rate of solution polymerization on temperature. Ferric ammonium sulfate, $10^{-6}$ mole/l.; hydrazine hydrate, 0.08 mole/l.; methyl methacrylate, 0.02 mole/l.; pH, 9.0.
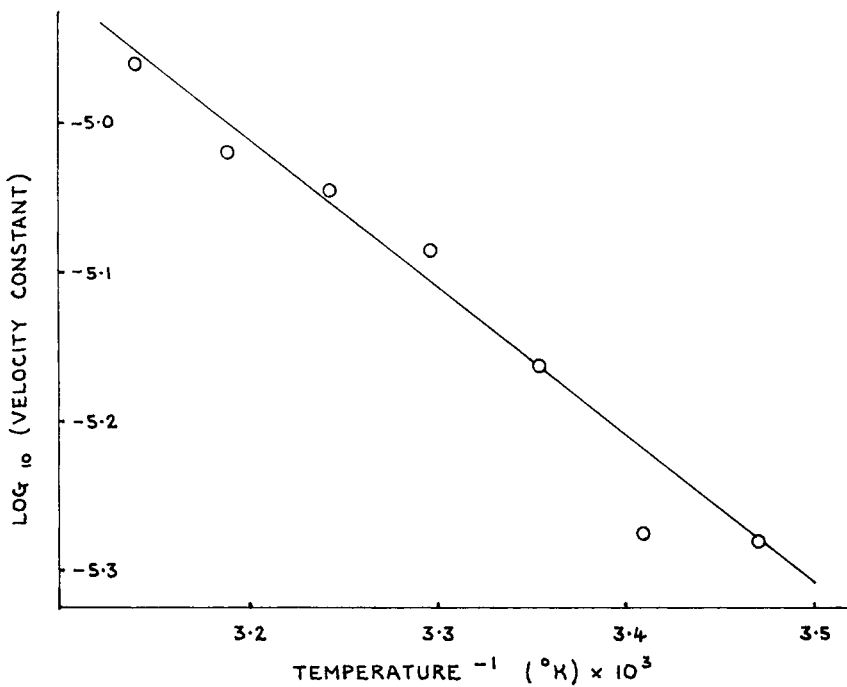


Fig. 4. Plot of logarithm of velocity constant against reciprocal of absolute temperature.
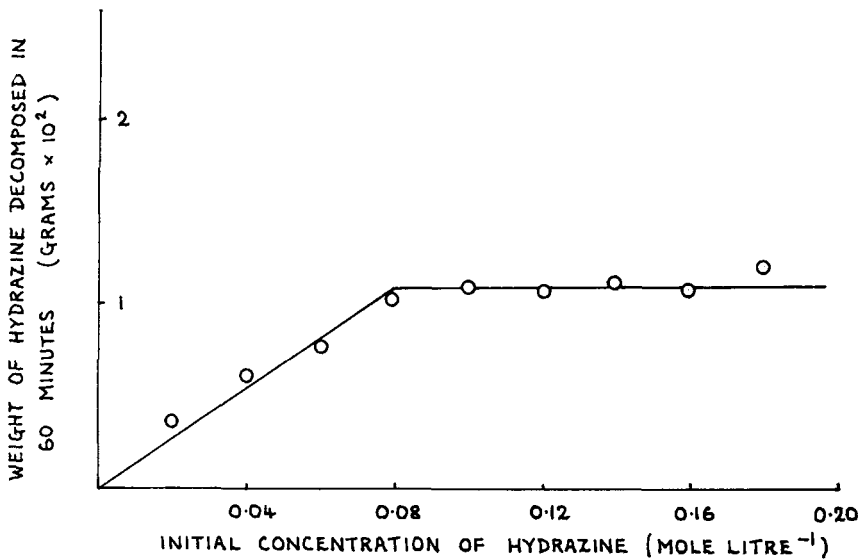
Fig. 5. Dependence of amount of hydrazine hydrate decomposed in 60 min on hydrazine hydrate concentration.  Ferric ammonium sulfate, $10^{-6}$ mole/l.;  methyl methacrylate, 0.02 mole/l.;  temperature, 30°C;  pH, 9.0.
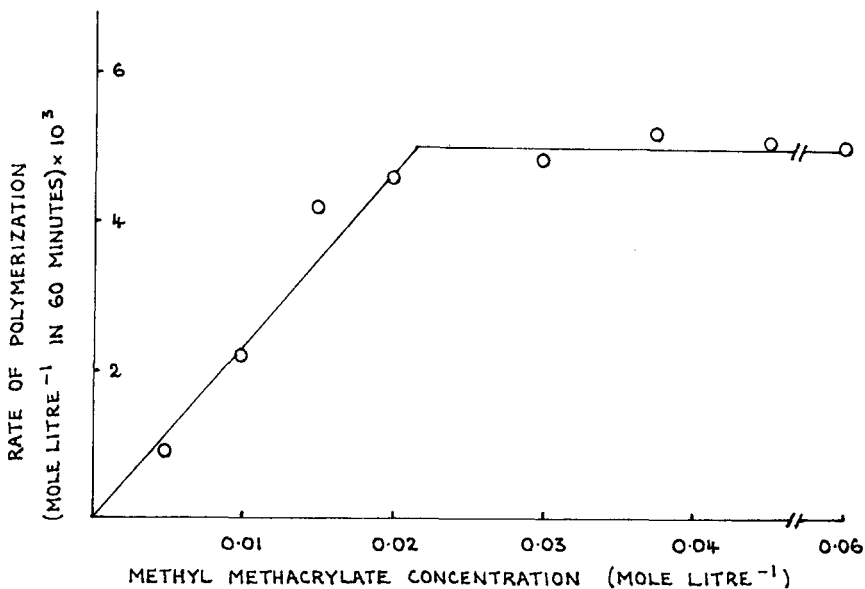


Fig. 6. Dependence of amount of polymer formed in 60 min on methyl methacrylate concentration.  Ferric ammonium sulfate, $10^{-6}$ mole/l.;  hydrazine hydrate, 0.08 mole/l.;  temperature, 30°C;  pH, 9.0.

is constant except at low hydrazine concentrations, the type of behavior to be expected for a surface-catalyzed decomposition. The rate of polymerization (not illustrated) showed parallel behavior, with the onset of constant rate occurring at the same hydrazine concentration (0.08 mole/l.).

**Variation of Initial Monomer Concentration.** At monomer concentrations greater than 0.02 mole/l., the rate of polymerization is independent of initial monomer concentration (Fig. 6, extent of conversion after 60 min was again used as a measure of reaction rate). This is once again typical of a surface reaction. Adsorption of monomer onto the hydroxide surface was demonstrated by shaking monomer solution of known concentration with a known amount of ferric hydroxide suspension at pH 9 and centrifuging the mixture. The supernatant liquor was analyzed for monomer, and a 10% decrease in monomer concentration was observed.

The behavior of this system is closely similar to the manganic hydroxide system. Rate of decomposition of hydrazine and rate of polymerization are both zero order, except at very low concentrations, suggesting that the initiation occurs on the hydroxide surface. In the case of the manganic system, this has been confirmed[9] by a polymerization below the saturation solubility, when the hydrazine decomposition became first order. This behavior has also been observed with the cupric/hydrazine system.[10] It was not feasible to perform a similar experiment in the ferric case because of the extremely low solubility of ferric hydroxide.

## References

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