The Manganic Hydroxide–Hydrazine Hydrate System as an Initiator of Vinyl Polymerization

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Synopsis

The reaction of hydrazine hydrate with manganic hydroxide and its application to the solution polymerization of methyl methacrylate has been studied. The kinetic evidence suggests that the hydrazine and the monomer are both adsorbed on the surface of the manganic hydroxide sol and that the decomposition of the hydrazine and the polymerization of the methyl methacrylate follow zero-order kinetics. The rate of polymerization increases slowly with increasing temperature, the activation energy for the polymerization being 4.9 ± 0.2 kcal/mole.

INTRODUCTION

The cupric sulfate–hydrazine hydrate system as an initiator of vinyl polymerization in aqueous solution has been the subject of several investigations[1–3] and has been found not to take place below pH 6. The present work deals with the reaction of hydrazine hydrate with manganic hydroxide and its application to the solution polymerization of methyl methacrylate. It has been reported[4] that potassium permanganate and hydrazine hydrate react in acid media, so the aim of this investigation was to ascertain whether the manganic hydroxide–hydrazine hydrate system was a suitable initiator of polymerization over a wide pH range.

EXPERIMENTAL

The experimental procedure was similar to that reported previously.[2] The apparatus consisted of eight tubes immersed in a constant temperature bath which was maintained at 30°C. Each tube was fitted with a condenser and a gas inlet tube. Oxygen was supplied to all the tubes from the same cylinder with the aid of an eight-piece manifold.

Manganic hydroxide was prepared in situ from a solution of manganous sulfate (analytical reagent grade). The pH of the solution was raised to 9.5 by the addition of 1 ml of 0.01 mole/l. sodium hydroxide solution when manganous sulfate was hydroxylated to manganous hydroxide. Oxygen was bubbled through this solution for 1 hr to effect a rapid quantitative conversion of the manganous hydroxide to manganic hydroxide.[5] At lower

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pH values, the conversion is extremely slow and nonquantitative, so that, in the experiments in which the polymerization was performed in solutions of pH less than 9.5, the pH of manganous sulfate solution was first raised to 9.5, and oxygen was bubbled through the solution for 1 hr after which the pH was adjusted to the required value.

The reaction mixture used was as follows: x ml of 0.125 mole/l. methyl methacrylate solution; y ml of 1 mole/l. hydrazine hydrate solution; z ml of standard manganous sulfate solution; 1 ml of 0.01 mole/l. sodium hydroxide solution; and $50 - (x + y + z + 1)$ ml deionized water. The pH of the final reaction mixture was 9.5 ± 0.1.

Oxygen bubbling was stopped immediately after the addition of the hydrazine hydrate solution; otherwise, long induction periods were obtained.

RESULTS

The results are shown graphically in Figures 1–6.

DISCUSSION

When oxygen was bubbled through the reaction mixture during the polymerization, induction periods of irreproducible lengths were obtained. However, when bubbling was stopped immediately after the addition of hydrazine hydrate solution, the induction periods became much shorter and on occasion disappeared completely. There was no change in the rate of polymerization from that obtained in the presence of oxygen bubbles under a given set of conditions.

The induction periods must be a result of radical scavenging by oxygen.

Since there is no report in the literature of the saturation solubility of manganic hydroxide, this was determined from conductivity measurements using a Wayne-Kerr Universal Bridge and a Jones-Bollinger conductivity cell. The value obtained was 10^{-7} mole/l. In all the polymerization experiments, concentrations of manganic hydroxide greater than this were always used so that the manganic hydroxide was present as a sol or as a flocculent precipitate according to its concentration.

At a constant manganic hydroxide concentration of 8×10^{-5} mole/l., the following holds true:

(a) The hydrazine decomposition follows zero-order kinetics above a hydrazine concentration of 0.02 mole/l. (Fig. 1); the corresponding rates of polymerization show a similar dependence on the hydrazine concentration. This, together with the immediate decrease in the concentration of hydrazine when it is added to the reaction mixture, indicate that the hydrazine is adsorbed onto the surface of the insoluble manganic hydroxide.

(b) The rate of polymerization is independent of the concentration of methyl methacrylate above 0.02 mole/l. methyl methacrylate. This suggests that the monomer is adsorbed on the surface of the hydroxide, and this was verified by shaking a solution of the monomer with a precipitate of
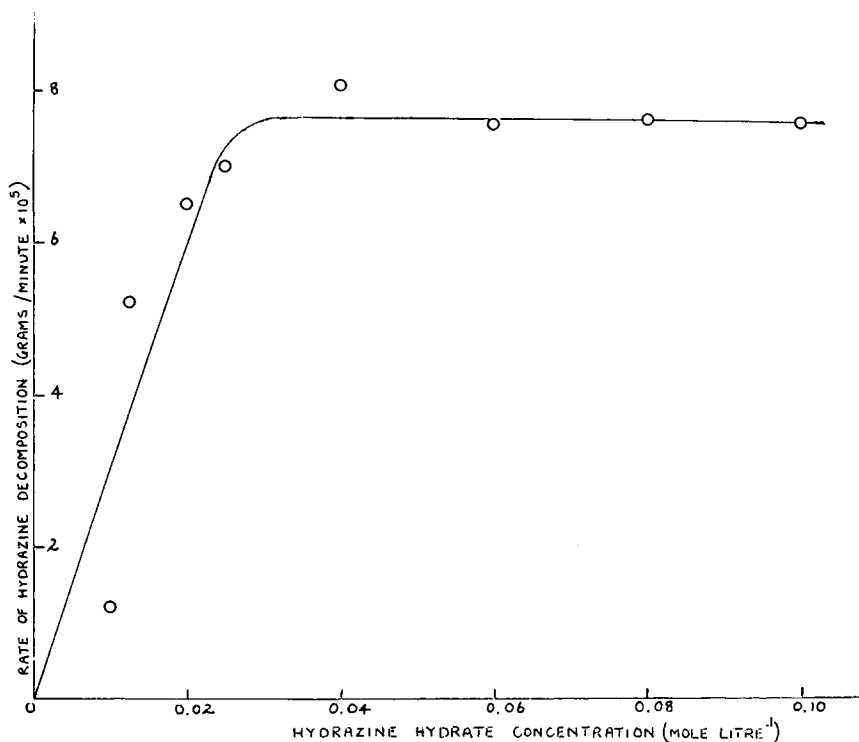
Fig. 1. Dependence of the rate of decomposition of hydrazine on the concentration of hydrazine: 8×10^{-5} mole/l. manganic hydroxide, 0.02 mole/l. methyl methacrylate.

manganic hydroxide and determining the concentration of methyl methacrylate remaining in solution after the precipitate was separated from it by centrifuging. A decrease in the concentration of monomer was noted. The percentage conversion of monomer to polymer during the course of the polymerization is directly proportional to the time of the reaction (Fig. 2), a typical feature of a zero-order reaction.

(c) The rate of polymerization decreases with decreasing pH while the length of the induction period increases; e.g., at pH 7.5 it was 2 hr and at 7.2 it increased to over 4 hr. In order to determine the minimum pH at which the polymerization proceeds, reaction mixtures were prepared ranging in pH from 2 to 7 and the polymerization allowed to continue for 16 hr. The percentage conversion of monomer to polymer decreased rapidly with decreasing pH; e.g., it was 60% at pH 7 and only 6% at pH 4.5. At pH values less than 4, no hydrazine decomposition and no polymerization occurred over a 16-hr period.

(d) The rate of polymerization varies with temperature as shown in Figure 3. This figure also illustrates the reproducibility of the rates of polymerization. Since the polymerization is zero order, this is then equivalent to the velocity constant of the overall reaction. An overall
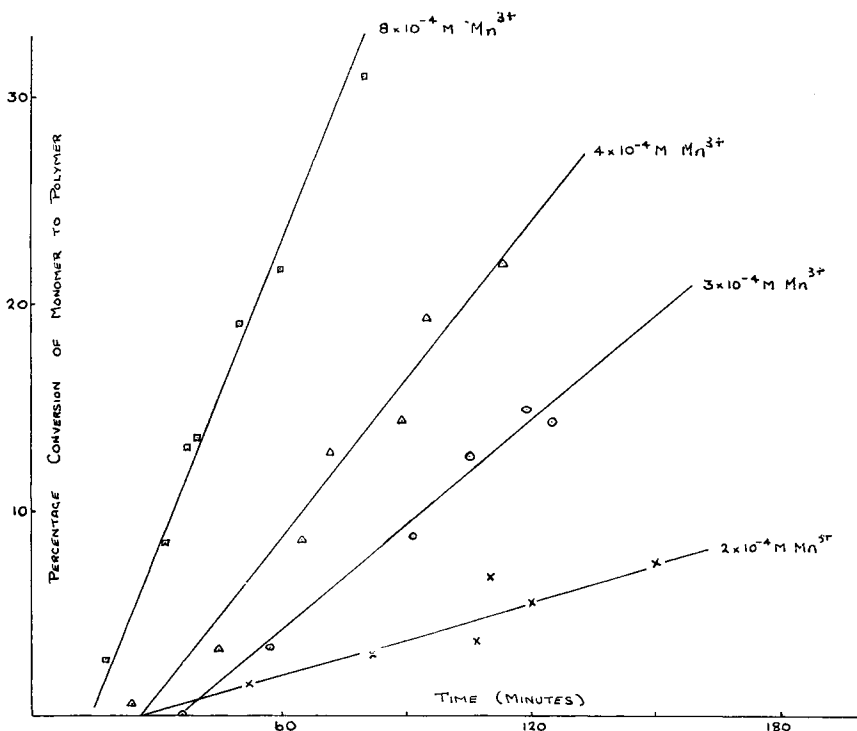
Fig. 2. Typical plot showing the conversion of monomer to polymer over a 2-hr period at different manganic ion concentrations at 30°C: 0.02 mole/l. methyl methacrylate, 0.08 mole/l. hydrazine hydrate.

activation energy of 4.9 ± 0.2 kcal/mole can be calculated from the slope of the line in the plot of log velocity constant versus reciprocal of absolute temperature (Fig. 4). The rate of hydrazine decomposition appears to be independent of temperature over the range 0–50°C. This is a typical feature of a surface-catalyzed reaction, the decomposition of the hydrazine into initiating radicals having an extremely low activation energy.

In Figure 5, the portion AB of the graph shows that the polymerization increases with increasing concentration of manganic hydroxide while the rate of decomposition of hydrazine shows a corresponding increase (Fig. 6, portion ab). At B, Figure 5, the rate of polymerization reaches a maximum after which it falls with increasing concentration of the hydroxide. The concentration of the hydroxide at B (2.136×10^{-5} mole/l.) corresponds to the saturation solubility of manganous hydroxide[6] so that, along the portion AB, i.e., at concentrations below the saturation solubility of manganous hydroxide, hydrazine is adsorbed on the surface of the insoluble manganic hydroxide sol particles and the manganic hydroxide is reduced to soluble manganous hydroxide. The latter is rapidly reoxidized to insoluble manganic hydroxide. However, once the saturation solubility of the manganous hydroxide has been exceeded, insoluble manganic hydroxide will be
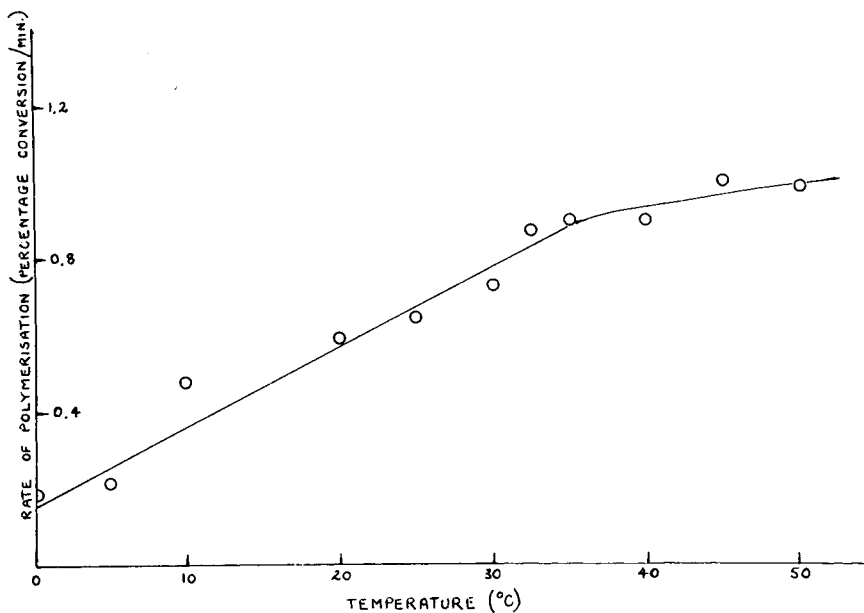
Fig. 3. The dependence of the rate of polymerization on temperature: 8×10^{-5} mole/l. manganic hydroxide, 0.02 mole/l. methyl methacrylate, 0.08 mole/l. hydrazine hydrate.
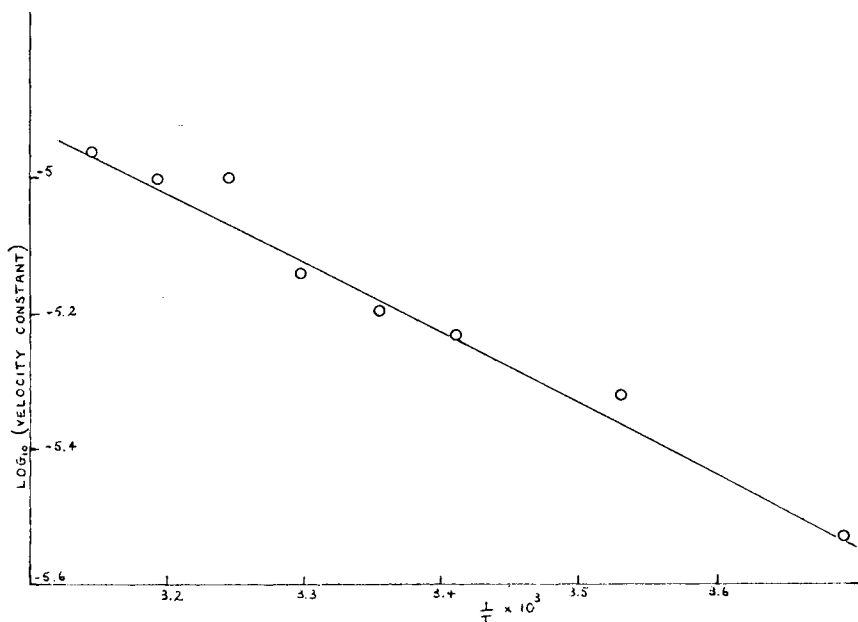

Fig. 4. Plot of the logarithm of the velocity constant against the reciprocal of the absolute temperature.

converted to insoluble manganous hydroxide by the action of the hydrazine. Hence, along section BC of the curve (Fig. 5), the amount of solid material present is continuously increasing with increasing concentration of the hydroxide. Although we have succeeded in polymerizing methyl methacrylate in solution using an initiator, manganous hydroxide and hydrazine in the absence of oxygen, we do not consider this to be the dominating reaction in the presence of oxygen because of the extremely rapid conversion of manganous hydroxide to manganic hydroxide in alkaline solution.
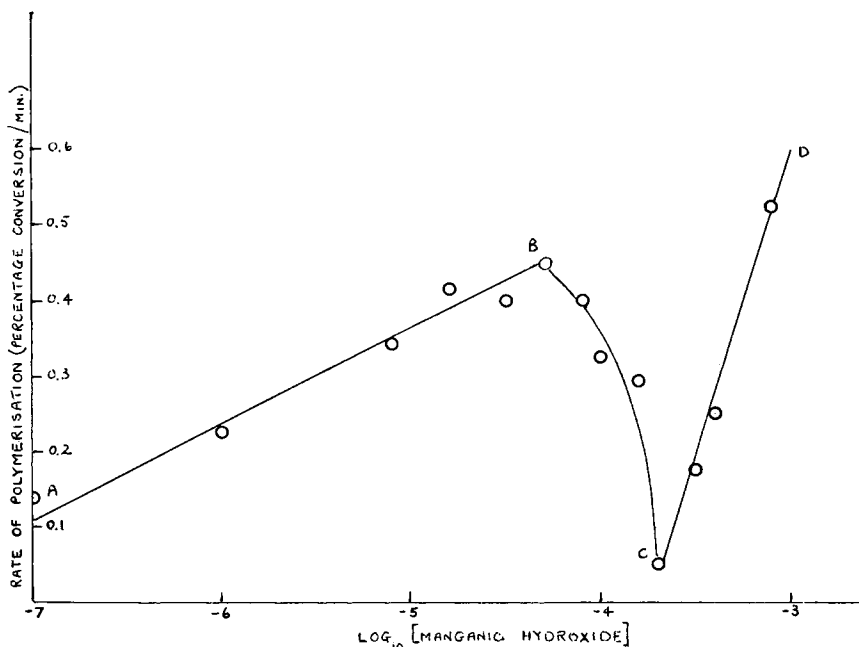

Fig. 5.   Dependence of the rate of polymerization on the concentration of manganic hydroxide: 0.08 mole/l. hydrazine hydrate, 0.02 mole/l. methyl methacrylate.

The decrease in the rate of polymerization along BC, as was suggested with the cupric sulfate–hydrazine hydrate initiating system,[2] can be attributed to the adsorption of primary radicals and their mutual annihilation on the surface of the precipitating hydroxide. Over the concentration range represented by BC in Figure 5, the rate of hydrazine decomposition increases only very slightly with increasing concentration of the hydroxide (Fig. 6, bc). However, at a manganic hydroxide concentration of 3 × 10^{-4} mole/l., the rate of hydrazine decomposition starts to increase markedly with increasing concentration of hydroxide with the corresponding increase in the rate of polymerization (Fig. 5, CD). At these concentrations, the manganic hydroxide is present in the form of a heavy, flocculant precipitate with a large surface area which results in adsorption and subsequent decomposition of large amounts of hydrazine.

In conclusion, the role of the surface present can be assessed. The manganic hydroxide–hydrazine reaction occurs on the surface of the insoluble hydroxide and the polymerization which occurs as a result of this increases in rate until the saturation solubility of the manganous hydroxide is reached. The extra surface area produced is sufficient for a drop in the
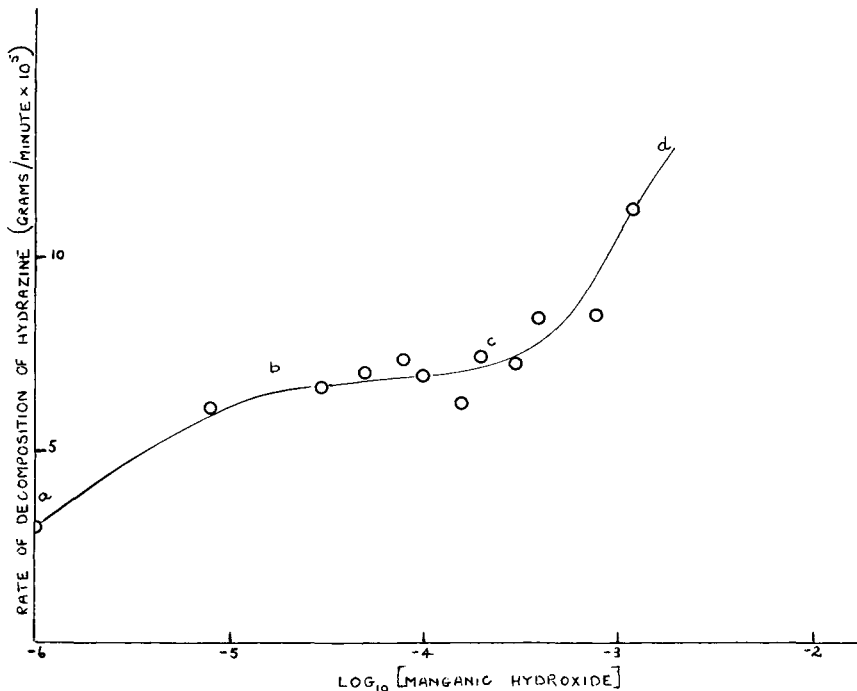

Fig. 6. Dependence of the rate of decomposition of hydrazine on the concentration of manganic hydroxide: 0.08 mole/l. hydrazine hydrate, 0.02 mole/l. methyl methacrylate.

polymerization rate to occur, probably as a result of adsorption of initiating radicals on this surface. In the presence of a heavy, flocculant precipitate of manganic hydroxide there is increased adsorption of hydrazine with a resultant increase in polymerization rate. The monomer is adsorbed on the surface of the manganic hydroxide sol and polymerization follows zero-order kinetics.

References

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