

The Manganic Hydroxide–Hydrazine System as an Initiator of Vinyl Polymerization. III. The Emulsion Polymerization of Methyl Methacrylate

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Synopsis

Emulsion polymerization of methyl methacrylate with the manganic hydroxide–hydrazine system has been studied. An attempt was made to corroborate earlier evidence that the initiation may involve a surface reaction on an insoluble manganese compound. The surface area of the manganic hydroxide was varied, and the effect of this variation on the rate of decomposition of hydrazine was examined. A correlation was found between the polymerization rate and the surface area of the precipitate.

INTRODUCTION

Emulsion polymerization of methyl methacrylate with the manganic hydroxide–hydrazine system as an initiator has been studied. Previous workers^{1–6} have suggested that in this system the manganese is precipitated as manganic hydroxide and that initiation takes place on the surface of this hydroxide. These workers believe that a surface reaction is involved for the following reasons: (a) A suitable precipitate of the insoluble metal hydroxide was present. (b) Adsorption of hydrazine onto the insoluble metal hydroxide occurred. When hydrazine is added to the reaction mixture, there is an immediate decrease of its concentration due to this adsorption onto the metallic hydroxide. (c) Adsorption of monomer onto the surface of the manganic hydroxide was verified by shaking a solution of the monomer with a precipitate of manganic hydroxide and determining the concentration of methyl methacrylate in solution after the manganese ions were separated from it by centrifugation. A decrease in the concentration of monomer was noted. (d) The hydrazine decomposition follows zero-order kinetics above hydrazine concentrations of 0.02 mole/dm³. Zero-order kinetics are a feature of many surface reactions.

The conclusion of the previous workers that a surface reaction was involved was based on indirect evidence. The present work is a direct attempt to corroborate this suggestion by varying the surface area of the manganic hydroxide and to observe the effect of this variation on the rate of polymerization and on the rate of decomposition. The concentration of manganous sulfate was varied during the initial stage in which oxygen was passed through the solution to oxidize manganous ions to manganic ions. After the oxidation stopped, the required ingredients were used and nitrogen flow started. Polymerization was started with the addition of hydrazine solution.

* Dr. C. W. Brown died in tragic circumstances on 25th July 1977. This work is dedicated to the memory of Dr. Brown, a brilliant research worker and devoted teacher.

EXPERIMENTAL

The basic polymerization technique was the same as that used by Longbottom.⁴⁻⁶ The technique was modified at the oxidation stage by varying the concentration of manganous sulfate, as shown in Table I. The concentration of manganous sulfate and the total amounts of ingredients used in this polymerization were kept finally constant.

The standard reaction mixture was as follows: 22.5 g distilled methyl methacrylate; 65 cm³ deionized water; 5 cm³ 0.02 mole/dm³ manganous sulfate; 50 cm³ 0.0576 mole/dm³ sodium dodecyl sulfate; 15 cm³ 0.4 mole/dm³ sodium hydroxide; and 12 cm³ 0.165 mole/dm³ hydrazine hydrate.

The percentage conversion was calculated from the formula

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

where R is the weight of residue, T is the total weight of all ingredients (based on 100 parts monomer), S is the weight of sample taken, and N is the total weight of nonvolatile nonpolymer components (based on 100 parts monomer). Percentage conversion was plotted against time, and the rate of polymerization was obtained from the straight-line portion of the graph. The rate of polymerization was plotted against the concentration of manganous sulfate and is shown in Figure 1.

The test for the decomposition of hydrazine in the polymerization was followed by withdrawing the required amount of the polymerization mixture at regular intervals of time after polymerization had started. Concentrated hydrochloric acid and chloroform were added to the sample and the mixture was treated with potassium iodate solution. The endpoint was rather difficult to discern because of masking by precipitating soap. However, with practice this difficulty could be minimized, and consistent results were obtained. The decomposition of hydrazine was plotted against time, and the adsorption of hydrazine on the insoluble manganic hydroxide was calculated by extrapolating the straight line. When hydrazine is added to the reaction mixture there is an immediate fall in hydrazine concentration due to its adsorption on the surface of the manganic hydroxide.^{4,5} This is followed by a slow decrease resulting from slow decomposition.

TABLE I

Concentration of manganous sulfate $\times 10^3$, moles/dm ³	Adsorption of hydrazine $\times 10^5$, moles	A_{m_1} surface area, ^a m ²
1.50	3.75	4.51
2.50	4.35	5.24
4.00	3.78	5.75
6.60	5.12	6.16
13.30	5.21	6.27

^a A_{m_1} refers to hydrazine hydrate with $M = 50.06$ and $\rho = 1.03$.

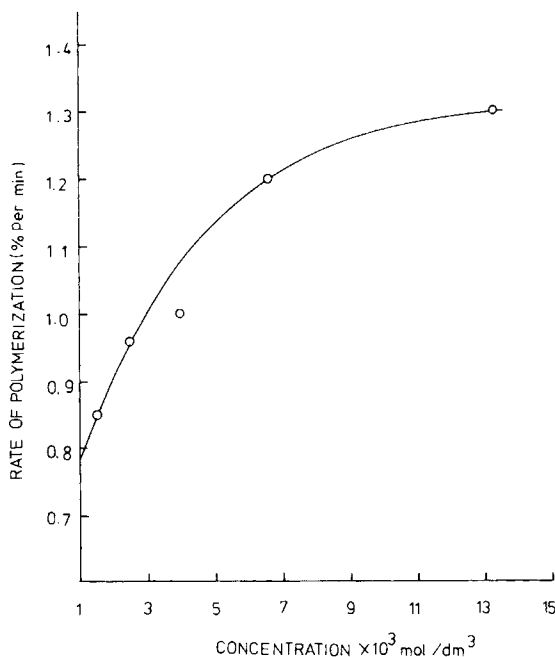


Fig. 1. Rate of polymerization vs concentration of manganese sulfate at the oxidation stage.

RESULTS AND DISCUSSION

It was observed that the rate of polymerization is higher when a higher concentration of manganese sulfate is used at the oxidation stage (remembering that the manganese sulfate concentration during subsequent polymerization was the same in all cases). The increased rate of polymerization at higher manganese sulfate concentration may be the result of an increased surface area of the insoluble manganic hydroxide due to the formation of smaller particles. The manganic hydroxide-hydrazine (initiation) reaction occurs on the increased surface of the insoluble manganic hydroxide, and the rate of polymerization is thus increased. It was also observed that the higher concentration of manganese sulfate gives higher adsorption of hydrazine, presumably due to the larger surface area. The rate of decomposition increases owing to increased adsorption of hydrazine on the larger surface area. The influence of the surface area can be assessed for both adsorption and decomposition of hydrazine.

The surface areas of various manganese concentrations are calculated from the formula⁷

$$S = (X_m/M)NA_m$$

where M is the molecular weight of the adsorbate; N is Avogadro's number; X_m is the monolayer capacity of the adsorbent, that is, the quantity of adsorbate which can be adsorbed by 1 g of the adsorbent in the complete monolayer; A_m is dependent on the way in which the molecules are packed on the surface in the completed monolayer:

$$A_m = (1.091M/\rho N)^{2/3}$$

where ρ = density of the adsorbate. Using the adsorption of hydrazine, the

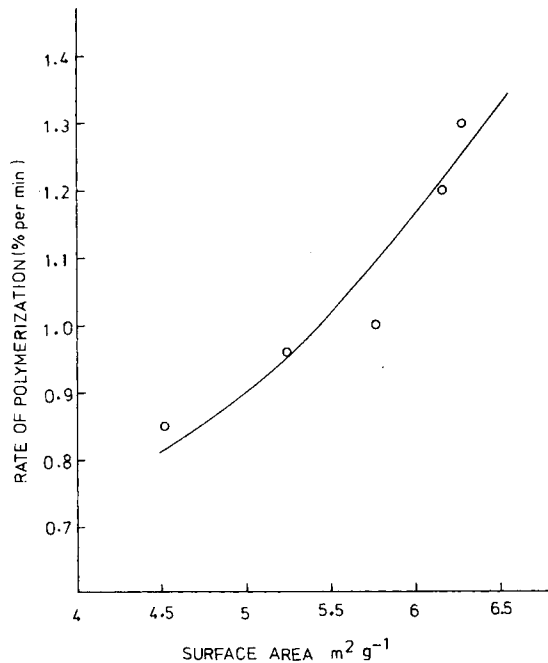


Fig. 2. Rate of polymerization vs surface area of manganic hydroxide.

surface area of manganic hydroxide calculated for each concentration of manganous sulfate is shown in Table I and is plotted against rate of polymerization in Figure 2. The rate of polymerization within experimental error is proportional to the surface area of the manganic hydroxide.

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