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

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Synopsis

The reaction between hydrazine hydrate and manganic hydroxide has been studied as an initiator for the emulsion polymerization of methyl methacrylate. The system has proved to be effective, and polymerization occurs at favorable rates over a wide temperature range extending from below 10°C to over 50°C. The pH range, however, is rather limited, the most effective value being 9. The main features of the initiator's behavior are similar to those found previously in the corresponding solution polymerization and are explained on the basis of a surface reaction between the hydrazine and the insoluble hydroxide. A complicating feature is the reaction between hydrazine and monomer, which exerts an inhibiting influence.

INTRODUCTION

The cupric sulfate–hydrazine hydrate system as an initiator of vinyl polymerization in both aqueous solution and emulsion has been the subject of a number of investigations.[1-7]   More recently, in part I of this report, the use of the manganic hydroxide–hydrazine hydrate system as an initiator of vinyl polymerization in aqueous solution has been investigated.[8]   The present communication is concerned with the application of this manganese system to the polymerization of methyl methacrylate under emulsion conditions.   Some comparisons are made between the manganese and cupric systems.

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.

Manganous Sulfate.   Analytical reagent grade was used, at least 97% pure, containing not more than 0.005% heavy metals.

Sodium Dodecyl Sulfate. Sodium dodecyl sulfate obtained from the
Sigma Chemical Company, Ltd., specified as 99.9% pure, was used.

METHOD

The experimental procedure was a modified version of that used by Bond
and Lee[7] in their study of the cupric sulfate–hydrazine hydrate–oxygen
initiating system. The apparatus consisted of a 250-ml three-necked,
round-bottomed flask fitted with gas inlet tube, condenser, stirrer, and also
a narrow bore tap through which samples of the reaction mixture were ex-
tracted by means of a hypodermic syringe and needle. The apparatus
was immersed in a constant temperature ($\pm 0.1°C$) water bath which was
maintained at 30°C, except where the influence of temperature on reaction
rate was being investigated.

The standard reaction mixture was: 22.5 g methyl methacrylate; 46.0
ml 0.16 mole/l. sodium dodecyl sulfate; 5.0 ml 1.0×10^{-1} mole/l. manga-
nous sulfate; 12.0 ml 1.0 mole/l. hydrazine hydrate; and 64.5 ml deionized
water. The pH of the resultant mixture was 9.5. At this pH, in the
presence of oxygen, the manganese is present as manganic hydroxide.[10]

Deionized water, 20 ml, heated to near boiling, was added to the flask
containing the manganous sulfate solution, and oxygen was bubbled
through for 1 hr. After the oxygen bubbling was stopped, the soap solution
and the remaining deionized water (both saturated with nitrogen at the
temperature of the bath) were added. This was followed by addition of
monomer. The mixture was stirred vigorously for 5 min to homogenize the
system, after which the stirring rate was reduced to 7 rps. Nitrogen was
then passed into the atmosphere above the mixture at 2 bubbles/sec, and
this was maintained for the remainder of the experiment. Polymerization
was started by addition of the hydrazine hydrate solution (also nitrogen
saturated at bath temperature) by means of a syringe through the narrow
bore tap. This addition was carried out over a period of 5 min in order to
obtain reproducible results. Addition of the hydrazine all at once results
in a lower rate of polymerization. Presumably, in the latter case (as has
been observed[11] with hydrogen peroxide under similar circumstances), high
local concentrations of radicals are formed leading to mutual annihilation.

In those experiments in which a pH of less than 9.5 was used, the pH of
the mixture was adjusted to 9.5 (by addition of sodium hydroxide solution)
prior to the oxygen bubbling, ensuring that the reaction between the oxygen
and the manganese was complete. The pH of the final mixture was ad-
justed to the required region by a suitable addition of hydrochloric acid to
the hydrazine before this was added to the system. In this way, any varia-
tion in the rate of polymerization resulting from pH change would be limited
to that caused by the effect of pH on the manganic hydroxide–hydrazine
reaction.

Samples were withdrawn at intervals of time during the course of the
reaction and, after weighing and quenching with a 1% solution of hydro-
quinone in acetone, were dried to constant weight in an oven at 70°C.

The percentage conversion was calculated from the formula

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

where R = weight of residue, T = total weight of all ingredients (based on 100 parts monomer), S = weight of sample taken, and N = total weight of nonvolatile nonpolymer components (based on 100 parts monomer).

Percentage conversion was plotted against time for each reaction. S-shaped curves typical of emulsion polymerizations were obtained and the zero-order rates were calculated from the straight portions of the graphs. Samples of the reaction mixture, 5 ml, were also withdrawn for hydrazine analysis by the method reported previously.[7]

RESULTS AND DISCUSSION

Attempts to carry out the reaction under an atmosphere of pure oxygen resulted in no polymer being formed in a working period of time. Similarly, under nitrogen, no polymer was formed, and it was found that in order to obtain polymerization at reproducible rates, either a mixed gas (e.g., 10%
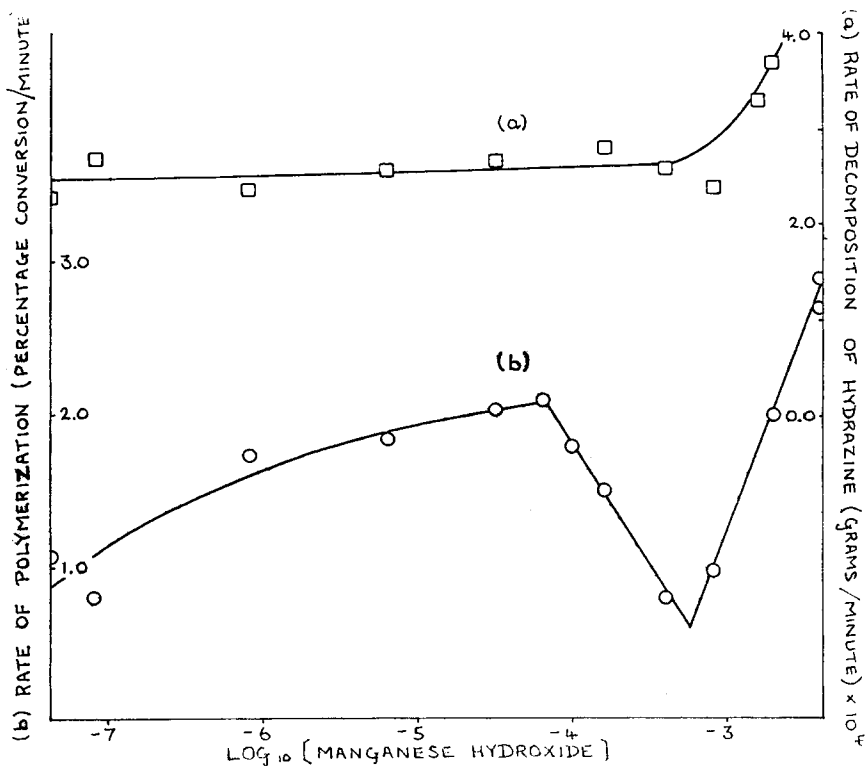

Fig. 1. Dependence of rate of hydrazine hydrate decomposition (a) and zero-order rate of polymerization (b) on manganese hydroxide concentration: hydrazine hydrate, 0.08 mole/l.; sodium dodecyl sulfate, 0.0576 mole/l.; methyl methacrylate, 15% (w/w); temperature, 30°C; pH, 9.5.
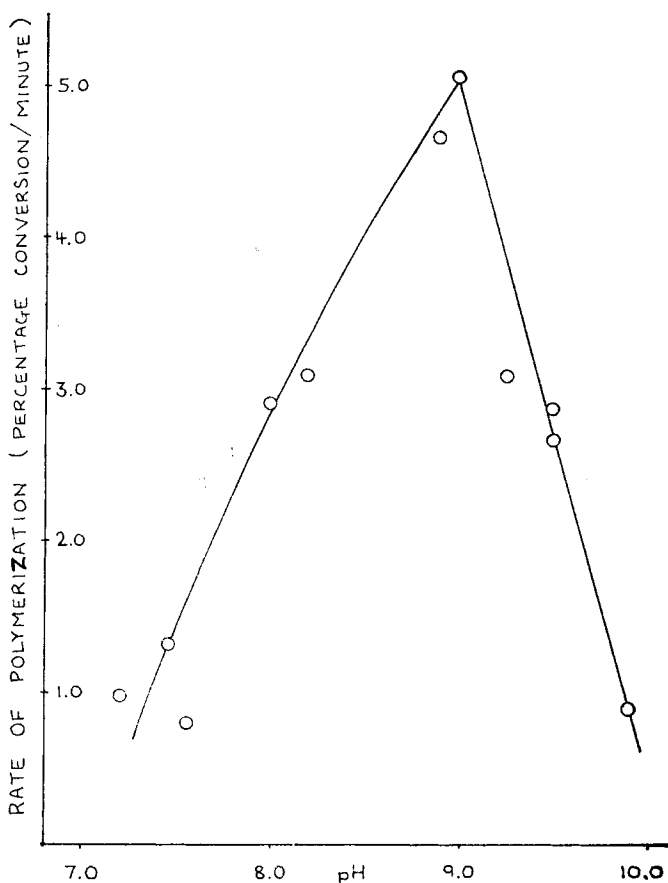
Fig. 2. Dependence of zero-order rate of polymerization on pH: manganese sulfate, 3.9×10^{-3} mole/l.; hydrazine hydrate, 0.08 mole/l.; sodium dodecyl sulfate, 0.0576 mole/l.; methyl methacrylate, 15% (w/w); temperature, 30°C.

oxygen and 90% nitrogen) had to be bubbled through or a fixed initial concentration of oxygen must be used. This paper deals mainly with the latter method in which the amount of oxygen present is determined by the volume of the aqueous phase saturated with oxygen during the bubbling period; and, unless stated otherwise, the following discussion relates to this system. Although irreproducible induction periods were observed, a number of experiments were performed using mixed gas bubbling when the effect of temperature was being studied.

The dependence of the rate of polymerization upon the manganese concentration is shown in Figure 1, which also gives the corresponding hydrazine decomposition rates. In the solution polymerization of methyl methacrylate by manganic hydroxide–hydrazine, curves of the same form were obtained, and the following explanation[8] was proposed to account for their shape. At low manganese concentrations, below the saturated solubility
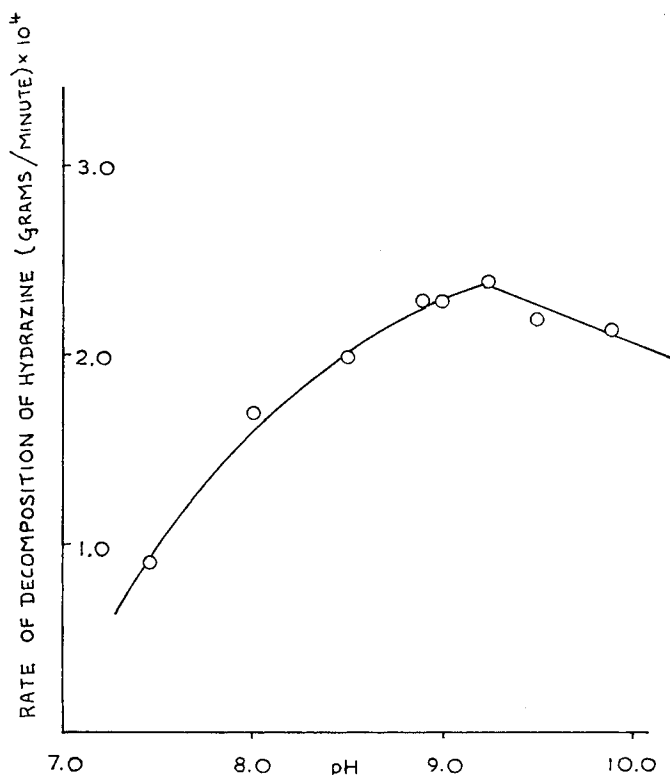
Fig. 3. Dependence of rate of hydrazine hydrate decomposition of pH: manganese sulfate, 3.9×10^{-3} mole/l.; hydrazine hydrate, 0.08 mole/l.; sodium dodecyl sulfate, 0.0576 mole/l.; methyl methacrylate, 15% (w/w); temperature, 30°C.

of manganous hydroxide ($\sim 2 \times 10^{-5}$ mole/l.), the rate of polymerization and the rate of hydrazine decomposition increase with increasing manganese concentration. In this region, the manganese is present as a manganic hydroxide sol, and the hydrazine reacts on the surface of these particles forming radicals and soluble manganous hydroxide which is then rapidly reoxidized to insoluble manganic hydroxide. At higher maganese concentrations, increasing amounts of insoluble manganous hydroxide will be present, offering increased opportunity for mutual annihilation on its surface. At the same time, the number of radicals produced remains approximately constant (vide the constant rate of hydrazine decomposition in this region), and so fewer radicals are available for initiation and the rate of polymerization is lowered. At still higher concentrations, the manganese is present in the form of a flocculant precipitate, offering an increased reaction surface which results in an increased rate of hydrazine decomposition and an increased rate of polymerization.

In the present work, the circumstances are essentially similar, and the same explanation is likely to apply. The main difference between the curves obtained in the solution and emulsion polymerizations, respectively,

is that in the latter case the maximum and minimum points occur at higher manganese concentrations, approximately double the corresponding value of the solution results.   A similar contrast was observed[7] between solution and emulsion polymerization of methyl methacrylate initiated by cupric sulfate and hydrazine.   The shift of the curve to higher manganese concentrations can be explained by adsorption of manganese ions onto the micelles, resulting in an increased solubility of the adsorbed ion.   This effect has
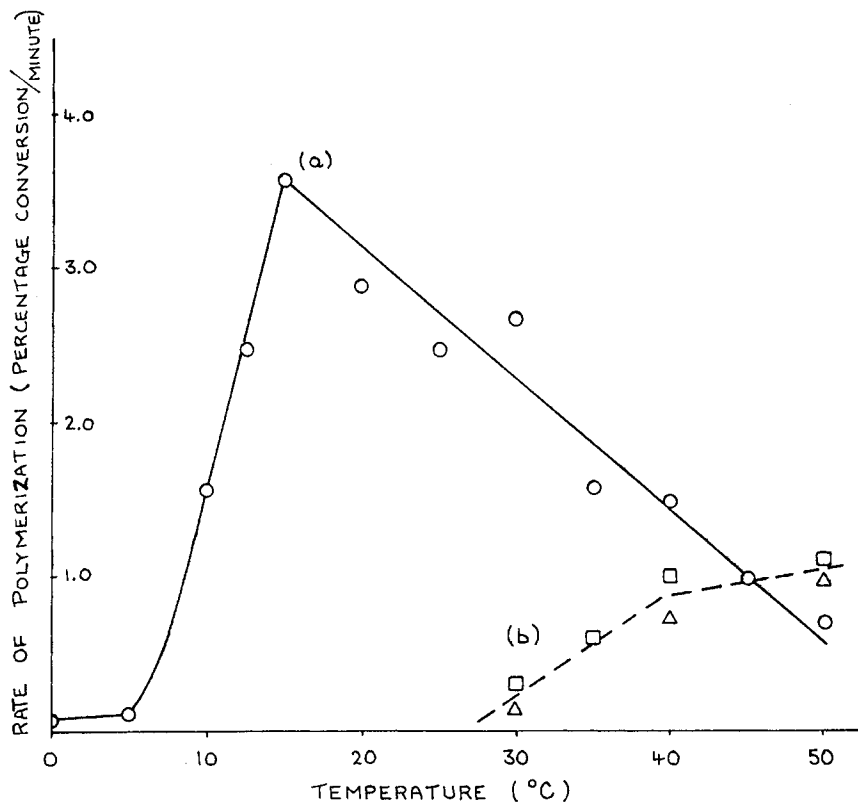

Fig. 4. Dependence of zero-order rate of polymerization using initial oxygen saturation (a) and 5% oxygen and 10% oxygen gas mixtures (b) on temperature: manganese sulfate, 3.9×10^{-3} mole/l.; hydrazine hydrate, 0.08 mole/l.; sodium dodecyl sulfate, 0.0576 mole/l.; methyl methacrylate, 15% (w/w); pH, 9.5; (□) 10% oxygen; (△) 5% oxygen.

been observed by Kolthoff and Johnson.[15]   In the present instance, the increase in solubility caused by this adsorption of ions on the micelles means that the surface effects which bring about the changes in direction of the curve (Fig. 1b) occur at a higher manganese concentration than would be observed in the absence of adsorption.

    At a constant manganese concentration of 3.9×10^{-3} mole/l., the following holds true:
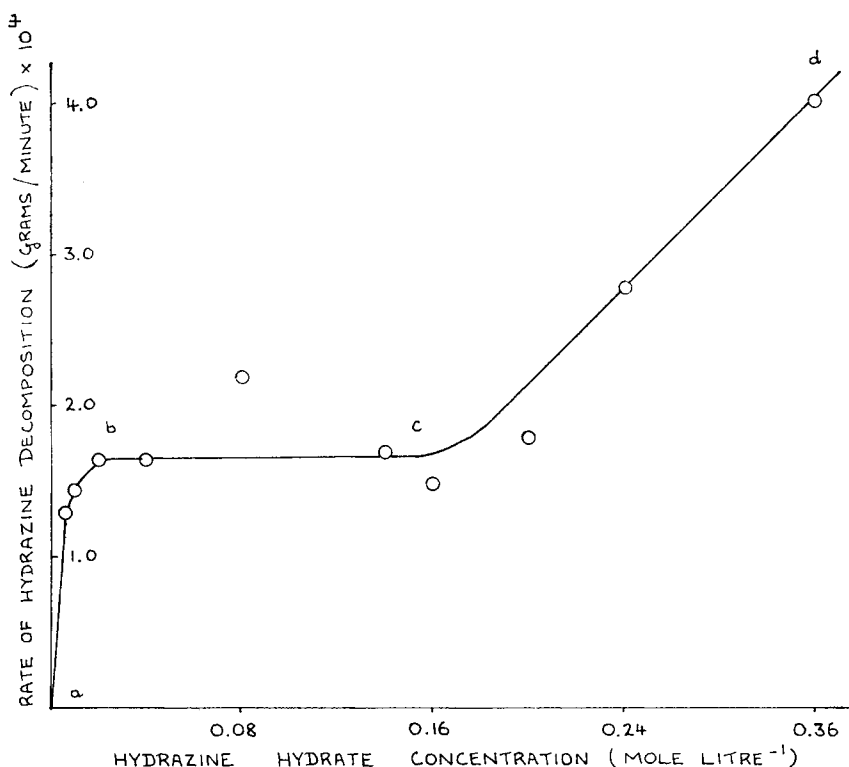
Fig. 5. Dependence of rate of hydrazine hydrate decomposition on hydrazine hydrate concentration: manganese sulfate, 3.9×10^{-3} mole/l.; sodium dodecyl sulfate, 0.0576 mole/l.; methyl methacrylate, 15% (w/w); temperature, 30°C; pH, 9.5.

(a) The dependence of the rate of polymerization upon the concentration of sodium dodecyl sulfate corresponds quite well with the theoretical predictions of Smith and Ewart[12] and of Gardon,[13] viz.:

$$\text{zero-order rate of polymerization } \alpha \text{ [emulsifier]}^{0.6}$$

The observed index of emulsifier concentration was 0.55. With continuous gas bubbling (10% oxygen, 90% nitrogen), however, the dependence index was found to be 0.18. These results are considered in more detail elsewhere.[14]

(b) The graph of rate of polymerization of methyl methacrylate versus pH (Fig. 2) takes the form of an inverted V, showing a maximum polymerization rate at pH 9.0. The variation of rate of hydrazine hydrate decomposition with pH shows a similar shape (Fig. 3), suggesting that the influence of pH is through the hydrazine hydrate–manganese reaction. The mechanism of the reaction between hydrazine and oxidizing agents is not well understood[16] but is known[17] to be strongly pH dependent. It is believed that the reactive species is the hydrazine molecule, and the fall in reaction rate as the pH is lowered from 9 is probably due to an increasing
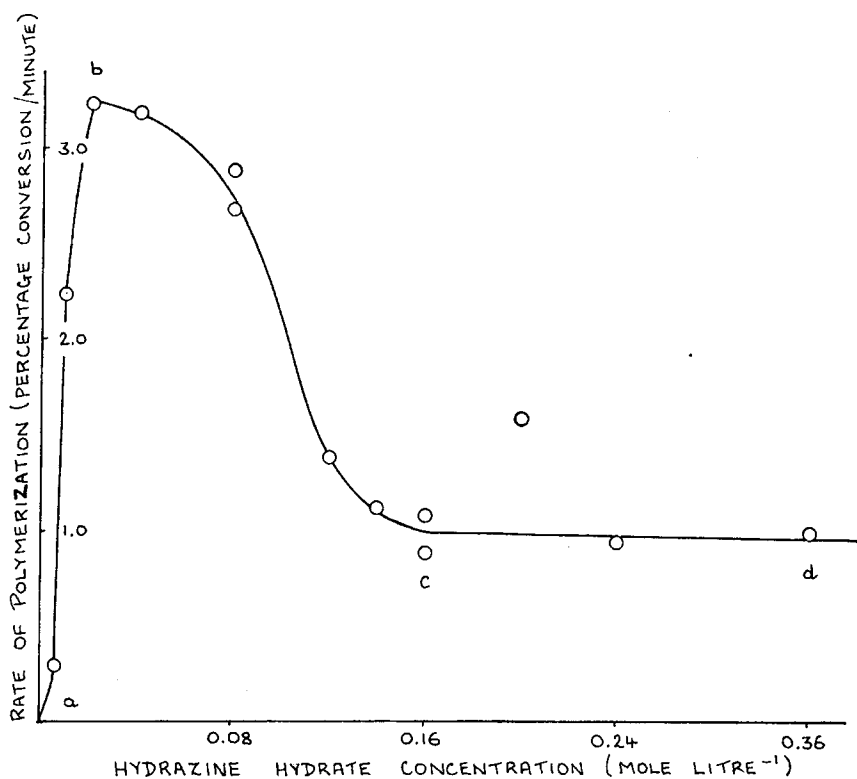
Fig. 6. Dependence of zero-order rate of polymerization on hydrazine hydrate concentration: manganese sulfate, 3.9×10^{-3} mole/l.; sodium dodecyl sulfate, 0.0576 mole/l.; methyl methacrylate, 15% (w/w); temperature, 30°C; pH, 9.5.

proportion of the hydrazine existing as the hydrazinium ion.   In the reaction between hydrazine and oxygen, the fall in reaction rate at high pH has been attributed[17] to changes in hydration and association of the reactive molecules.   Such an explanation may also apply to the hydrazine–manganese reaction although, in the absence of a detailed mechanism, a more direct influence of pH on reaction rate cannot be ruled out.

(c) The variation of zero-order rate of polymerization with temperature is shown, curve a in Figure 4.   It is unusual in that, after increasing with temperature in the usual way between 5°C and 15°C, the rate of polymerization falls when the temperature is raised to higher values.   The points on the "normal" part of the graph give an excellent Arrhenius plot, leading to an activation energy of 27.9 kcal/mole.

The fall in rate of polymerization at higher temperatures can be attributed to the diminished amount of oxygen present at the higher temperatures.   This explanation is supported by (1) admission of oxygen part way through a polymerization results in an increase in the reaction rate, and (2) experiments with continuous gas bubbling.   Instead of supplying oxygen to the system by means of saturating a fixed amount of manganous sulfate

solution, continuous bubbling of an oxygen–nitrogen mixture was used so that an excess of oxygen was always present. Mixtures containing 5% and 10% oxygen were used. In both cases (see Fig. 4b), the zero-order rate rises steadily with temperature, and there is no diminution in rate at the higher temperatures. These results give activation energies closely similar to the value of 27.9 kcal/mole obtained above. The values are somewhat higher than those quoted by other workers[7,9] for the emulsion polymerization of methyl methacrylate, viz., 23.7 and 24.4 kcal/mole, respectively.

It is interesting to note that the rate of polymerization with continuous gas bubbling is appreciably less than that obtained by the other technique. A reduction in zero-order rate by a factor of approximately 10 was observed at 30°C. A similar difference has been noticed in the hydrazine–copper initiating system.[18] It is presumably caused by retardation due to the excess oxygen present in the continuous bubbling systems.

Over the temperature range investigated, that rate of hydrazine hydrate decomposition was constant—a common feature of surface-catalyzed reactions.

(d) Figures 5 and 6 show the variation with hydrazine hydrate concentration of rate of hydrazine decomposition and rate of polymerization, respectively. The shape of these curves can be explained by consideration of the surface nature of the hydrazine–manganese reaction together with the possibility of reaction between hydrazine and methyl methacrylate. This reaction was demonstrated by Bond and Lee,[7] although the nature of the product was not elucidated. The most likely product of such a reaction is methacrylic hydrazide, a substance which has been obtained by Shvaika and Makarenko.[19] A sample of the hydrazide was prepared using their method, and its effect on the polymerization was examined. The hydrazide was found to exert a marked retarding influence (e.g., a hydrazide concentration of $0.001M$ reduced the rate of polymerization by almost 50%). At low hydrazide concentration, the retarding effect increased with increasing hydrazide concentration, but at higher hydrazide concentrations the effect levelled off and the rate of polymerization became constant. Under emulsion polymerization conditions, the hydrazine–monomer reaction will occur at all the hydrazine concentrations used but will be more significant at the higher values.

In Figure 5, the rate of hydrazine decomposition increases sharply in the region a–b due to increasing adsorption of hydrazine on the reactive surface. The reaction rate becomes constant (region b–c) when the surface is saturated. This situation is very similar to that observed in the solution polymerization of methyl methacrylate using the hydrazine–manganese initiator.[8]

The rate of polymerization (Fig. 6) shows an initial sharp rise (region a–b) corresponding to the increasing production of radicals by the initiator. In this region of low hydrazine concentration, the amount of hydrazide formed will be small, and its influence is also small. However, in region b–c, where the rate of radical formation is constant, the increasing amount of hydrazide formed (i.e., with increasing hydrazine concentration) will exert an in-

creasing influence on the rate of polymerization which therefore falls.   In the third region, c–d, the effect of the hydrazide has reached its limit, and the rate of polymerization remains constant.   In this region, the hydrazine–monomer reaction becomes sufficiently significant to produce an observable effect on the rate of hydrazine decomposition (Fig. 5, c–d), which therefore rises.

The general behavior of this initiator is thus broadly similar to that observed when it is applied to the solution polymerization of methyl methacrylate[8] and may be explained in a similar manner.   The initiator may find useful application in view of the appreciable rates of polymerization obtained at temperatures extending to less than 10°C.

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