NOTES

The Ferric Hydroxide-Hydrazine System as an Initiator of Vinyl Polymerization. II. The Emulsion Polymerization of Methyl Methacrylate

The polymerizations were carried out by the method described previously for the manganic hydroxide–hydrazine system,[1] with the oxidation stage omitted. Except where stated otherwise, the temperature was 35°C and the pH 8.6.

The results, depicted in Figures 1–6, show a pattern closely similar to those previously reported for the manganic hydroxide system in both solution[2] and emulsion[1] and for the ferric hydroxide–hydrazine system in solution,[3] and similar comments will, in general, be applicable. Discussion here is therefore confined to a brief comparison of the iron and manganese systems in solution, and in emulsion, polymerization.

In all cases, the rate of polymerization v log [metal hydroxide] curve (as in Fig. 1, lower curve) shows a fairly sharp maximum. For the two solution polymerizations, this maximum occurs at a metal hydroxide concentration corresponding to the saturation solubility of the lower hydroxide (1×10^{-5} mole/l. for ferrous hydroxide), whereas in the emulsion polymerizations, the maxima occur at appreciably higher metal hydroxide concentrations. This difference in the position of the maximum has been attributed to adsorption of ions onto the micelles.[2,4,5] In all cases, the shape of the hydrazine decomposition curve (Fig. 1, upper curve) is similar.
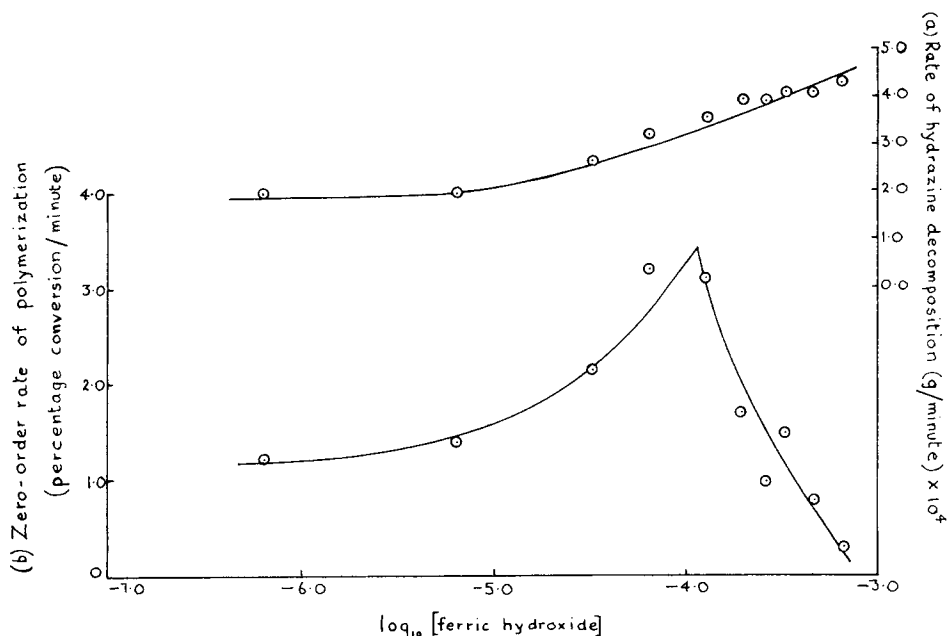

Fig. 1. Dependence of (a) rate of hydrazine decomposition and (b) zero-order rate of polymerization on ferric hydroxide concentration: hydrazine hydrate, 0.093 mole/l.; sodium dodecyl sulfate, 0.0576 mole/l.; methyl methacrylate, 15% w/w; pH, 8.6; temperature, 35°C.
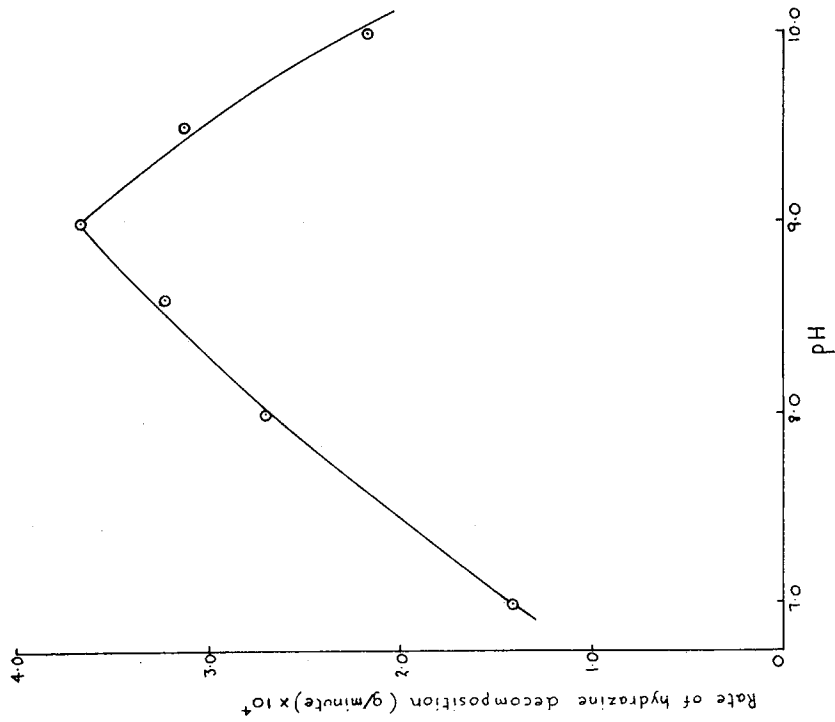
Fig. 3. Dependence of rate of hydrazine decomposition on pH: iron concentration, 6.3×10^{-5} mole/l.; hydrazine hydrate, 0.093 mole/l.; sodium dodecyl sulfate, 0.0576 mole/l.; methyl methacrylate, 15% w/w temperature, 35°C.

Fig. 2. Dependence of zero-order rate of polymerization on pH; iron concentration, 6.3×10^{-5} mole/l.; hydrazine hydrate, 0.093 mole/l.; sodium dodecyl sulfate, 0.0576 mole/l.; methyl methacrylate, 15% w/w; temperature, 35°C.
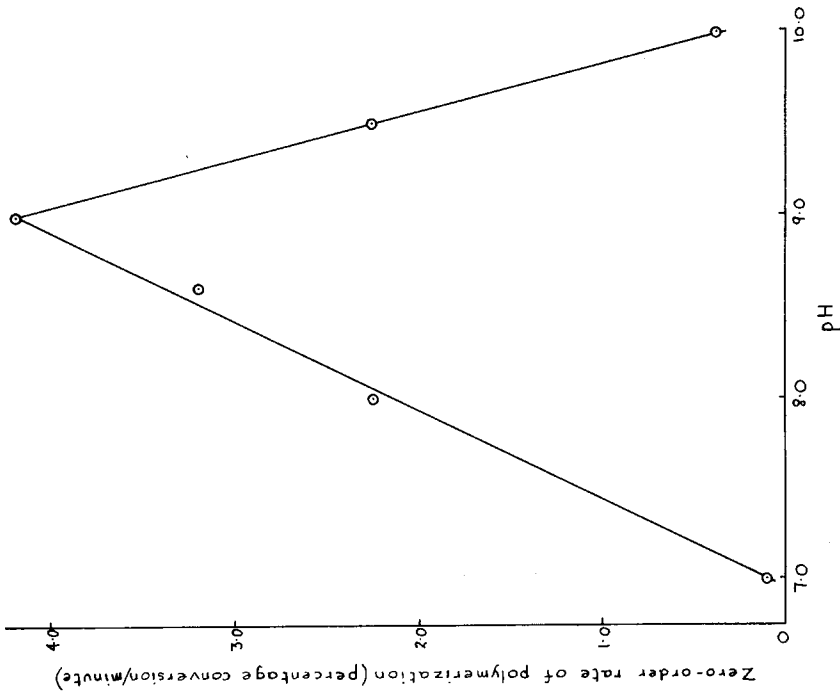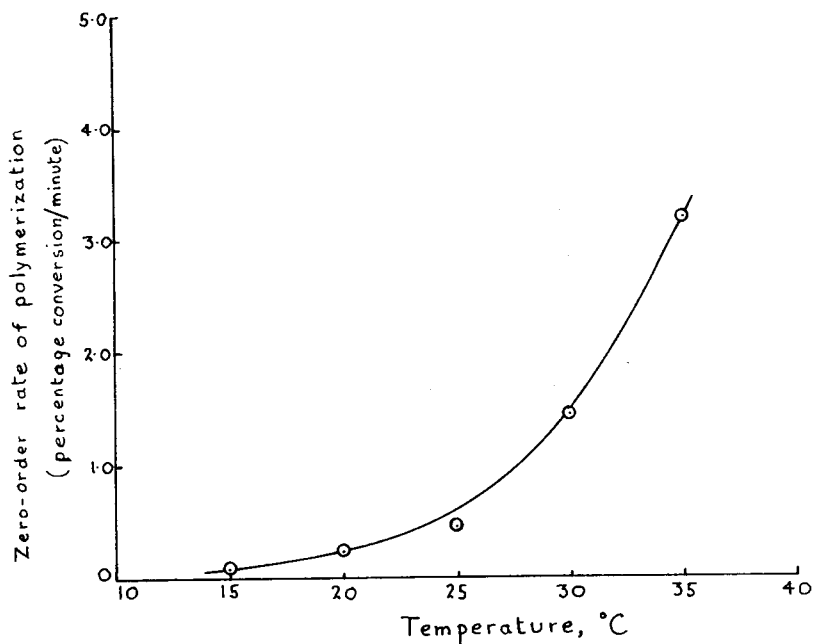
Fig. 4. Dependence of zero-order rate of polymerization on temperature: iron concentration, 6.3×10^{-5} mole/l.; hydrazine hydrate, 0.093 mole/l.; sodium dodecyl sulfate, 0.0576 mole/l.; methyl methacrylate, 15% w/w; pH, 8.6.
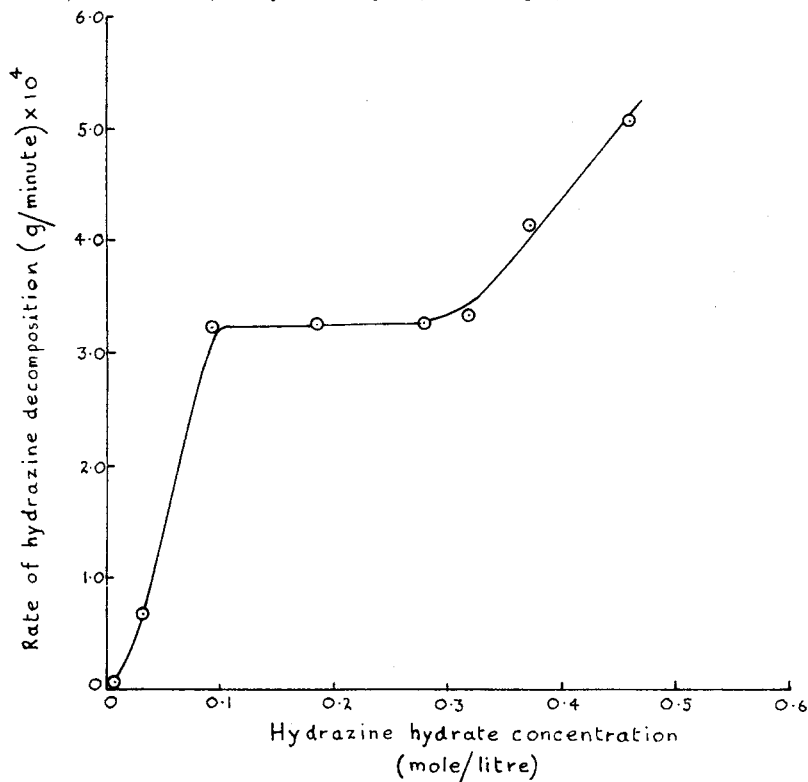

Fig. 5. Dependence of rate of hydrazine decomposition on hydrazine hydrate concentration: iron concentration, 6.3×10^{-5} mole/l.; sodium dodecyl sulfate, 0.0576 mole/l.; methyl methacrylate, 15% w/w; pH, 8.6; temperature, 35°C.

The variation of rate of polymerization with pH (Fig. 2) is virtually identical in the two emulsion systems, both showing a very sharp maximum at around pH 9 with essentially zero rate below pH 7 and above pH 10. A maximum at pH 9 is also shown by the rate of hydrazine decomposition v pH curve (Fig. 3). In contrast, in the solution polymerizations, both the rate of polymerization and the rate of hydrazine decomposition continue to increase over the entire pH range studied.

The variation of zero-order rate of polymerization with temperature is shown in Figure 4. These results yield an overall activation energy of 31.7 kcal/mole, slightly higher than the value for the corresponding manganese system. For both initiators in solution polymerization, activation energies are in the range of 4.5–5.0 kcal/mole, within the range expected for solution polymerization of methyl methacrylate. In all of the cases studied, the rate of hydrazine decomposition was independent of temperature.

The variation with hydrazine concentration of the rate of hydrazine decomposition and of the zero-order rate of polymerization are depicted in Figures 5 and 6, respectively. The behavior closely resembles that shown by the manganese hydroxide–hydrazine system.[1]
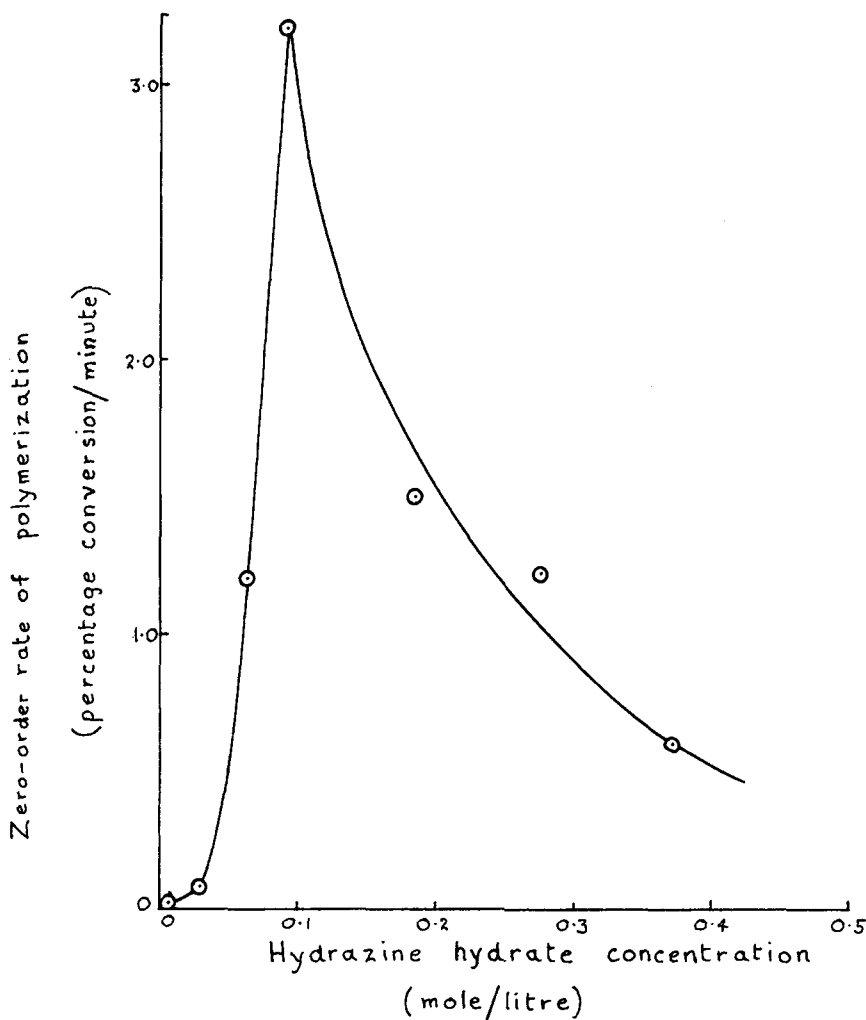

Fig. 6. Dependence of zero-order rate of polymerization on hydrazine hydrate concentration: iron concentration, 6.3×10^{-5} mole/l.; sodium dodecyl sulfate, 0.0576 mole/l.; methyl methacrylate, 15% w/w, pH, 8.6; temperature, 35°C.

It is clear that the general behavior of the ferric hydroxide–hydrazine initiating system closely parallels that of the corresponding manganese system. Moreover, the differences, in each case, between their behavior in solution and in emulsion are also very similar. Comparable behavior is shown in the cupric–hydrazine system,[4,6,7] although in this instance the correspondence is rather less close.

References

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