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

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Synopsis

The behavior of the emulsifier sodium dodecyl sulfate and electrolyte sodium hydroxide was studied at the oxidation stage and beyond in the emulsion polymerization of methyl methacrylate initiated by the manganic hydroxide–hydrazine hydrate system. From the rate of polymerization and from the adsorption of hydrazine it was shown that addition of emulsifier is more effective at the oxidation stage than after. But the reverse is obtained with the electrolyte. The effect of hydrazine concentration was also studied. The results are explained on the basis of a surface reaction between hydrazine hydrate and the insoluble manganic hydroxide.

INTRODUCTION

A metal hydroxide–hydrazine hydrate system as an initiator in the emulsion polymerization of methyl methacrylate has been studied by previous workers.[1–6] They believe that a surface reaction is involved in this system. In the present work the surface reaction has been studied using manganous sulfate with emulsifier and sodium hydroxide at the oxidation stage. Experiments were also performed with various concentrations of hydrazine hydrate in order to observe its effect on manganic hydroxide. It has been reported[4,5] that in this system manganous sulfate is converted to manganic hydroxide and that hydrazine decomposes on the surface of the manganic hydroxide.

EXPERIMENTAL

Preparation and Purification of Materials

Methyl Methacrylate. This was distilled under reduced pressure under nitrogen. The pure methyl methacrylate was stored at 10°C.

Sodium Dodecyl Sulfate. This was obtained from Sigma Chem. Co., St. Louis, Missouri, U.S.A. The solution was prepared by dissolving in deionized water. The purity of this emulsifier was specified at 99.9%.

Hydrazine Hydrate. The solution was prepared by dissolution in nitrogen-saturated deionized water and its concentration determined by titration with potassium iodate solution in the presence of chloroform and concentrated hydrochloric acid.[7]

* Deceased.

Method

The basic polymerization technique employed is the same as that used by Longbottom[4,5] and is a modified version of that used by Bond and Lee[2,3] in their study of the cupric sulfate–hydrazine hydrate-initiated system. The reaction flask containing the required amount of manganous sulfate solution was immersed in a constant temperature at $30 \pm 0.1°C$. The standard mixture was as follows: 22.5 g distilled methyl methacrylate, 65 cm^3 nitrogen-saturated deionied water, 50 cm^3 0.0576 mol/dm^3 emulsifier (sodium dodecyl sulfate), 15 cm^3 0.04 mol/dm^3 sodium hydroxide, 12 cm^3 0.08 mol/dm^3 hydrazine hydrate, and 5 cm^3 0.02 mol/dm^3 manganous sulfate.

In the initial stage of the polymerization oxygen was bubbled through the manganous sulfate solution for 1 hr to convert manganous to manganic state. After oxidation was stopped, the nitrogen flow was started and maintained for the remainder of the experiment. The required amount of emulsifier, nitrogen-saturated deionized water, and sodium hydroxide was added to the flask. These were followed by the monomer, dropwise from a separating funnel, and the whole mixture was stirred vigorously for about 10 min to homogenize the system after which the stirring was reduced. The polymerization was started by the addition of hydrazine.

The above technique was modified at the oxygen bubbling stage using the above standard mixture in the following ways (the concentration of the ingredients and the total volume of the standard mixture remained the same in each polymerization technique):

a. **Use of Water.** 5 cm^3 of 0.02 mol/dm^3 manganous sulphate solution were diluted with 20 cm^3 of water before oxidation started. Those volumes of water were compensated for by appropriate variation in the volume of water added after oxidation has been completed.

b. **Use of Soidum Hydroxide.** 5 cm^3 of 0.02 mol/dm^3 manganous sulfate solution was diluted with 15 cm^3 of 0.04 mol/dm^3 sodium hydroxide and 5 cm^3 of water.

c. **Use of emulsifier.** 5 cm^3 of 0.02 mol/dm^3 manganous sulfate solution was diluted with 50 cm^3 of 0.0576 mol/dm^3 sodium dodecyl sulfate.

d. **Use of Emulsifier and Sodium Hydroxide Solution.** 5 cm^3 of 0.02 mol/dm^3 manganous sulfate was diluted with 25 cm^3 of 0.1152 mol/dm^3 sodium dodecyl sulfate, 15 cm^3 of 0.04 mol/dm^3 sodium hydroxide, and 10 cm^3 water.

A further series of experiments studying the decomposition of hydrazine during

TABLE I

Experimental conditions[a]	Rate of polymerization, % min	Adsorption of hydrazine hydrate, moles $\times 10^5$	Surface area, m^2
A	1.00	4.78	5.75
B	0.78	3.93	4.73
C	1.42	7.34	8.84
D	0.97	4.01	4.83

[a] A = 5 cm^3 0.02 mol/dm^3 manganous sulfate and 20 cm^3 water; B = 5 cm^3 0.02 mol/dm^3 manganous sulfate, 15 cm^3 0.04 mol/dm^3 sodium hydroxide and 5 cm^3 water; C = 5 cm^3 0.02 mol/dm^3 manganous sulfate and 50 cm^3 0.0576 mol/dm^3 sodium dodecyl sulfate; D = 5 cm^3 0.02 mol/dm^3 of manganous sulfate, 25 cm^3 0.1152 mol/dm^3 sodium dodecyl sulfate, 15 cm^3 0.04 mol/dm^3 sodium hydroxide, and 10 cm^3 water.

TABLE II

Initial concentration of hydrazine, $(mol/dm^3) \times 10^3$	Equilibrium concentration c of free hydrazine, $(mol/dm^3) \times 10^3$	Absorption of hydrazine y, $\times 10^5$ mol	c/y
5.83	5.37	7.77	11.80
8.78	8.26	8.88	15.88
11.23	10.68	9.39	19.40
14.40	13.68	0.57	24.71
17.56	17.00	9.57	30.35

polymerization were also carried out using the standard mixture with varying concentrations of hydrazine. The volume of hydrazine solution added for each experiment remained the same, but its concentration was changed. The percentage conversion obtained using techniques (a), (b), (c), and (d) was plotted against time for each reaction. The zero-order rate was calculated from the straight portion of the curve.

The hydrazine decomposed in the polymerization was analyzed by withdrawing the required amount of polymer mixture and titrating with potassium iodate solution in the presence of concentrated hydrochloric acid and chloroform. The amount of hydrazine decomposed was plotted against time, and the adsorption of hydrazine on the insoluble manganic hydroxide was calculated by extrapolating the straight line to zero time. The surface area[8] of the manganic hydroxide was calculated from the adsorption of hydrazine.

RESULTS AND DISCUSSION

Table I shows the rate of polymerization and the amount of hydrazine adsorbed. The highest rate of polymerization was obtained when emulsifier was
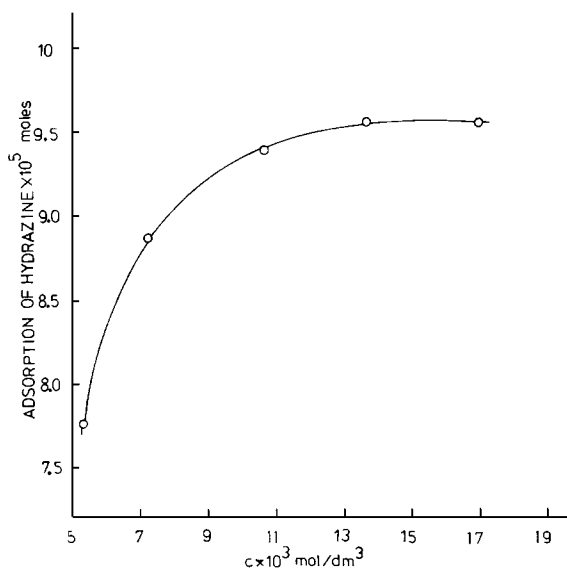

Fig. 1. Plot of adsorption of hydrazine vs equilibrium concentration c of free hydrazine.
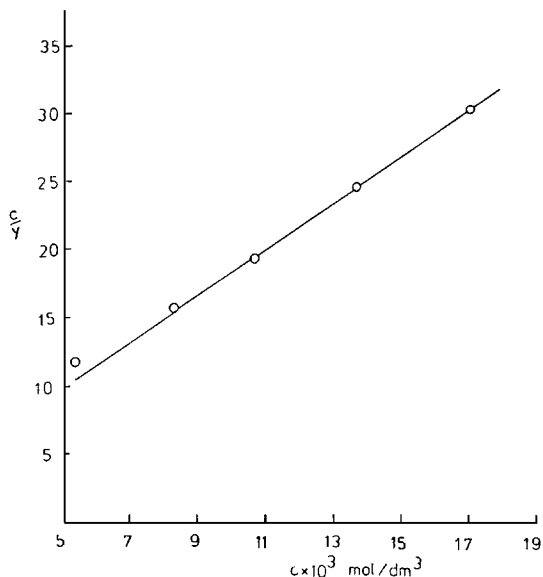
Fig. 2. Plot of c/y vs c (equilibrium concentration of free hydrazine) for adsorption of hydrazine.

used at the oxidation stage, not beyond. This may be the result of increased surface area of the insoluble manganic hydroxide due to the formation of smaller particles. The emulsifier probably stabilizes the particle surface and hence encourages the formation of smaller particles. Thus, emulsifier is more effective in promoting a larger surface area, as shown in Table I. The influence of a larger surface area can be assessed for both higher adsorption and decomposition of hydrazine. Increase in the rate of decomposition and adsorption due to the larger surface area increases the rate of polymerization.

The sodium hydroxide used at the initial stage of the polymerization (i.e., oxidation stage) depresses the rate of polymerization as well as the decomposition and adsorption of hydrazine. An increased rate of polymerization is obtained when it is used after oxidation has stopped. The following factors may be considered for the depression of the rate: (i) Addition of sodium hydroxide solution precipitates manganous hydroxide, which subsequently oxidizes to manganic; in this case precipitation precedes oxidation. (ii) It was observed with reference to Brown and Longbottom[5] that above pH 9 rate falls away rapidly and this was attributed[9] to change in hydration and association of the relative molecules; the addition of sodium hydroxide solution will lift the pH into this region. (iii) The addition of electrolyte, i.e., sodium hydroxide may produce a coagulating effect on the manganic hydroxide.

Table II shows the adsorption of hydrazine on manganic hydroxide at various concentrations of hydrazine. It has been observed that the adsorption of hydrazine increases initially and then becomes constant, as shown in Figure 1. This behavior can be explained by the surface nature of hydrazine–manganic hydroxide. When hydrazine is added to the reaction mixture there is an immediate decrease in hydrazine concentration due to its adsorption on the surface of the manganic hydroxide. With the increase in hydrazine concentration, the adsorption increases until the surface is saturated.

The data for the adsorption of hydrazine, shown in Table II, is plotted in Figure 2 according to the Langmuir adsorption isotherm whose equation[10] can be written as

$$c/y = 1/a + (b/a)c$$

where c is the equilibrium concentration of free hydrazine and y is the amount of hydrazine adsorbed. It can be concluded that the adsorption of hydrazine in this work follows the Langmuir adsorption isotherm.

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