

Sodium Bisulfite-Initiated Polymerization of Methyl Methacrylate in Aqueous Medium in the Presence of the Metal Oxides CuO and MnO₂

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Synopsis

Sodium bisulfite-initiated polymerization of methyl methacrylate (MMA) in water medium was carried out in the absence and in the presence of cupric oxide and manganese dioxide using various initiator concentrations at various temperatures ranging from 30° to 60°C. It seems that the metal oxide-water interface plays an important role, as it has been found that both oxides accelerate the rate of polymerization. Cupric oxide was found to be more effective than manganese dioxide. The cupric oxide was found to have nearly the same catalytic effect as the cuprous oxide, and manganese dioxide was found to be somewhat more effective than titanium dioxide. The initial rate of polymerization increased from 2.3×10^{-5} mole/(l. sec) to 3.4×10^{-4} mole/(l. sec) and to 6.6×10^{-5} mole/(l. sec) when the metal oxide concentration increased from 0 to 3 g/l. in case of cupric oxide and manganese dioxide, respectively. The initial rate of polymerization increased from 3.7×10^{-4} mole/(l. sec) to 4.2×10^{-4} mole/(l. sec) and from 7.2×10^{-5} to 2.2×10^{-4} mole/(l. sec) when the temperature was raised from 30° to 60°C in the presence of cupric oxide and manganese dioxide, (9 g/l.), respectively. Both the rate of polymerization and the number-average molecular weights were found to increase with increase in monomer concentration; the rate values were higher while the number-average molecular weights were lower in case of cupric oxide than in case of manganese dioxide. For example, the rate of polymerization increased from 2×10^{-5} mole/(l. sec) to 8.1×10^{-5} mole/(l. sec) and from 1.9×10^{-5} mole/(l. sec) to 6.9×10^{-5} mole/(l. sec); and the number-average molecular weight increased from 0.7×10^5 to 2.2×10^5 and from 1.5×10^5 to 4.9×10^5 in the presence of cupric oxide and manganese dioxide (10 g/l.), respectively, when the monomer concentration was increased from 23.5 g to 94 g/l. water. The apparent energy of activation for the polymerization of methyl methacrylate in water medium between 40° and 50°C was found to be 0.8 and 4.3 kcal/mole when using cupric oxide and manganese dioxide (9 g/l.), respectively.

INTRODUCTION

Polymerization of methyl methacrylate with lead dioxide as a heterogeneous catalyst was studied at 50°C in benzene. Lee¹ reported that lead dioxide polymerizes the methyl methacrylate by a radical mechanism, but it proved to be ineffective with respect to styrene and acrylonitrile. The rate of polymerization of methyl methacrylate was accelerated by the addition of dimethyl aniline to the reaction system.

It was also found that the sodium bisulfite-initiated polymerization of methyl methacrylate in water was catalyzed by soda lime glass.^{2,3} The iron oxide⁴ present in the sand as impurity proved to have a catalytic effect on the aqueous polymerization of methyl methacrylate. This led to the study of the effect of

ferric oxide on the sulfurous acid⁵ and the sodium bisulfite-initiated polymerization of methyl methacrylate.⁶

It was also reported that methyl methacrylate was polymerized in an aqueous solution of $O\text{---}NaHSO_3$ without stirring to obtain polymers of very high molecular weights. The polymerization took place not only in the aqueous phase, but also at the interphase between the water and monomer phases and also in the monomer phase. The polymerization in the monomer phase was very rapid when the concentration of the sodium bisulfite was more than 0.3%. The reaction was accelerated by the addition of small amounts of Cu^{2+} . In order to carry out the gel polymerization in the monomer phase when the polymerization is carried out using $O\text{---}NaHSO_3$ as initiator, it is necessary that the monomer is an α,β -carbonyl-conjugated olefin; as the monomer is relatively hydrophylic, if the oxygen atmosphere is displaced by nitrogen, the reaction system is slightly acidic.⁷

In a recent publication,⁸ the effect of cuprous oxide and titanium dioxide on the sodium bisulfite-initiated polymerization of methyl methacrylate in water medium was studied. In this work, the effect of cupric oxide and manganese dioxide on the aqueous polymerization of methyl methacrylate using sodium bisulfite as initiator was studied. However, the effect on the number-average molecular weight was also given.

EXPERIMENTAL

Materials

Methyl methacrylate was obtained by the thermal degradation of scrap polymer; the monomer was then dried by anhydrous sodium sulfate and fractionated by means of a fractionating column of about 15 theoretical plates; the fraction boiling between 100.0° and 100.5°C was collected.

Manganese dioxide was a technical powder from Chemische Fabrik Erich Nickel Struth-Schmalkalden (Thür); cupric oxide, a German powder for element analysis Formerly VEB Schering Aldershof. Sodium bisulfite was a product of El Nasr Pharmaceutical Chemical Co. ARE; the nonvolatile matter in each did not exceed 0.005%.

Polymerization Process

The polymerization was carried out in a 250-ml, well-stoppered conical flask put in an automatically controlled water bath. The weight of the metal oxide under consideration was put in the conical flask followed by a suitable amount of initiator, distilled water, and finally methyl methacrylate. The content of the conical was shaken five times in 3 sec every half hour.

The percentage of conversion to polymer was calculated in the same way mentioned in a previous publication.²

Extraction of Pure Poly(methyl Methacrylate)

A certain weight of the metal oxide polymer composite was soaked in benzene for 24 hr; the polymer solution was filtered. Sometimes, it was necessary to use

a laboratory centrifuge to facilitate the filtration. The polymer was then precipitated in methanol, filtered, and dried at 50°C in an electric oven.

Determination of Intrinsic Viscosity and Molecular Weight of Polymers

The intrinsic viscosity $[\eta]$ for each polymer was obtained by the usual method of extrapolation. Number-average molecular weights \bar{M}_n for poly(methyl methacrylate) were calculated from the $[\eta]$ values using the equation

$$\bar{M}_n = 2.8 \times 10^5 [\eta]^{1.32}$$

All viscosity measurements were performed at 35°C.⁸ Adsorption of nitrogen at -195°C was determined using a conventional volumetric apparatus.⁹

The monolayer capacities of the samples were determined using the BET equation,¹⁰ and the surface areas were calculated according to the corresponding relation:

$$\Sigma = \frac{V_m}{22,400} \times N \times A \times 10^{-20}$$

where Σ is the specific surface area expressed in square meters per gram; N is Avogadro's number; and A is the area in square angstroms covered by a nitrogen molecule (16.2 \AA^2).¹¹

RESULTS AND DISCUSSION

The effect of cupric oxide and of manganese dioxide on the polymerization of methyl methacrylate (10 g) in water (100 ml) at 40°C using NaHSO_3 as initiator (0.05 mole/l.) was studied, and the data are given in Table I and represented in Figure 1.

From Table I, it is seen that the initial rate of polymerization is increased with increase in cupric oxide or manganese dioxide. Cupric oxide increased the initial rate of polymerization to a larger extent than manganese dioxide. The initial rate of polymerization increased from 1.3×10^{-5} mole/(l. sec) to 13.8×10^{-5} and 38.9×10^{-5} when the metal oxide was increased from 0 to 9 g/l. in case of manganese dioxide and cupric oxide, respectively. On the contrary, the number-average molecular weights decreased with increase in metal oxide; the decreases in the number-average molecular weights are greater in case of cupric oxide. The

TABLE I
Effect of Metal Oxides on the Polymerization of Methyl Methacrylate

Oxide wt., g	Cupric oxide			Manganese dioxide		
	Initial rate $\times 10^5$, mole/(l. sec)	Conv., %	$\bar{M}_n \times 10^{-5}$	Initial rate $\times 10^5$, mole/(l. sec)	Conv., %	$\bar{M}_n \times 10^4$
0.0	1.3	26	11.4	—	—	—
0.3	33.9	92	3.0	6.6	73	43.9
0.5	36.6	92	2.5	12.2	77	42.6
0.9	38.9	92	2.1	13.8	69	37.7

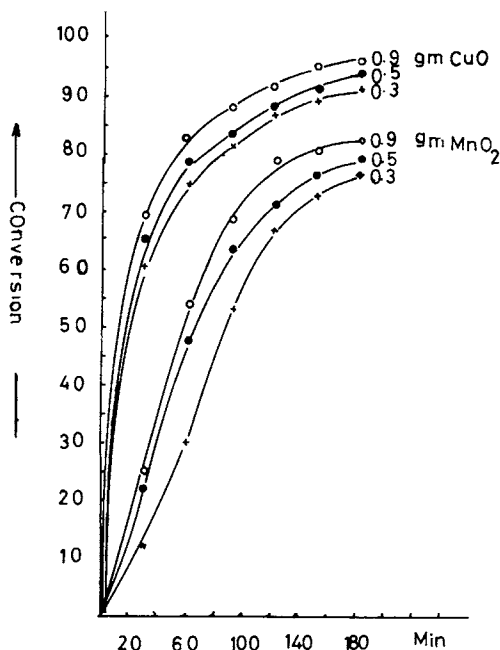


Fig. 1. Effect of metal oxides on rate of polymerization.

conversion percentages given in the tables are the values corresponding to the number-average molecular weights determined.

The effect of the initiator concentration on the polymerization of methyl methacrylate (10 g) in water (100 ml) in presence of 0.9 g metal oxide at 40°C was studied, and the data are given in Table II and represented in Figure 2.

From Table II, it is seen that both the initial rate (*I.R.*) of the polymerization and the obtained number-average molecular weights increase with increase in initiator concentration. In the absence of the metal oxide, the initial rate of polymerization increased from 0.8×10^{-5} mole/(l. sec) to 1.3×10^{-5} mole/(l. sec), while in case of cupric oxide, it increased from 30×10^{-5} to 38×10^{-5} mole/(l.

TABLE II
Effect of Initiator Concentration on Rate of Polymerization and on Average Molecular Weights

Initiator concn., mole/l.	MMA (alone)			MMA with cupric oxide			MMA with manganese dioxide		
	<i>I.R.</i> ^a × 10 ⁵ , mole/(l. sec)	Conv., %	\bar{M}_n × 10 ⁻⁵	<i>I.R.</i> × 10 ⁵ , mole/(l. sec)	Conv., %	\bar{M}_n × 10 ⁻⁵	<i>I.R.</i> × 10 ⁵ , mole/(l. sec)	Conv., %	\bar{M}_n × 10 ⁻⁵
0.02	—	—	—	23	77	0.68	3.9	26	1.34
0.03	0.8	12	—	30	82	0.92	5.5	29	1.66
0.04	1.0	13	—	34	82	1.31	7.2	26	1.95
0.05	1.3	26	11.4	38	82	2.1	13.9	25	2.59

^a *I.R.* = Initial rate.

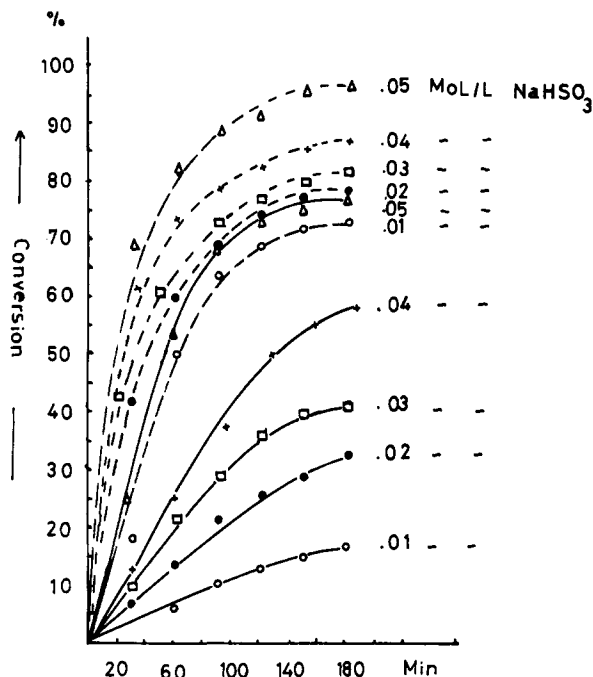


Fig. 2. Effect of initiator on rate of polymerization (9 g/l.): (---) CuO; (●—) MnO₂.

sec) and from 1.7×10^{-5} mole/(l. sec) to 2.6×10^{-5} mole/(l. sec) when the initiator concentration increased from 0.03 mole/l. to 0.05 mole/l.

The effect of increasing the amount of monomer on the polymerization rate and on the obtained number-average molecular weights was studied with and without using the metal oxide (10 g/l. water) at 40°C. The data are given in Table III.

From Table III, it is clear that both the rate of polymerization and the number-average molecular weights increase with increase in monomer concentration. In all systems, the polymerization occurs in a saturated aqueous methyl methacrylate solution. According to the literature, the saturation concentration is

TABLE III
Effect of Monomer Amount on Overall Rate of Polymerization (*O.R.*)
and on Number-Average Molecular Weight \bar{M}_n

[MMA], mole/l.	MMA alone			MMA with CuO			MMA with MnO ₂		
	<i>O.R.</i> × 10 ⁵ , mole/ (l. sec.)	Conv., %	\bar{M}_n × 10 ⁻⁵	<i>O.R.</i> × 10 ⁵ , mole/ (l. sec.)	Conv., %	\bar{M}_n × 10 ⁻⁵	<i>O.R.</i> × 10 ⁵ , mole/ (l. sec.)	Conv., %	\bar{M}_n × 10 ⁻⁵
0.235	1.7	79	2.7	2.0	94	0.7	1.9	86	1.5
0.470	1.9	43	4.6	4.1	92	1.2	3.7	85	2.5
0.705	2.1	33	6.7	6.0	92	1.9	5.5	85	3.7
0.94	2.3	26	11.4	8.1	93	2.2	6.9	80	4.9
1.175	2.3	21	19.0	9.9	91	2.4	8.3	76	7.1

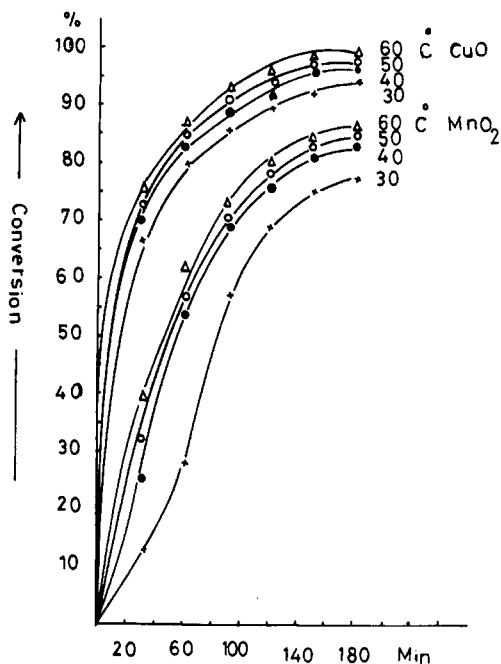


Fig. 3. Effect of temperature on rate of polymerization.

at 30°C 0.150 mole/l. and at 60°C, 0.149 mole/l. This assures the role played by the used metal oxides at the interfacial surface between them and the monomer. Although the specific surface of the manganese dioxide was greater (81.5 m²/g) than the cupric oxide specific surface (30 m²/g), cupric oxide, was yet found to be more effective than manganese dioxide.

On the one hand, the highest number-average molecular weights and the lowest overall rates are obtained in the absence of metal oxides.⁸ On the other hand, the highest overall rates and the lowest number-average molecular weights are those obtained with increase of cupric oxide. Moderate values of both are obtained when manganese dioxide is used.

The rates increased from 2.0×10^{-5} mole/(l. sec) to 9.9×10^{-5} mole/(l. sec) and from 1.9×10^{-5} mole/(l. sec) to 8.3×10^{-5} mole/(l. sec), and the number-

TABLE IV
Effect of Temperature on Initial Rate of Polymerization and Number Average Molecular Weight \bar{M}_n

Temp., °C	MMA alone			MMA with CuO			MMA with MnO ₂		
	Rate × 10 ⁵ , mole/(l. sec)	Conv., %	$\bar{M}_n \times 10^{-5}$	Rate × 10 ⁵ , mole/(l. sec)	Conv., %	$\bar{M}_n \times 10^{-5}$	Rate × 10 ⁵ , mole/(l. sec)	Conv., %	$\bar{M}_n \times 10^{-5}$
30	0.7	—	—	3.72	92	2.52	7.2	69	4.51
40	1.3	26	11.4	3.88	92	2.06	13.9	69	3.77
50	3.0	25	9.5	4.05	91	1.89	17.7	70	3.26
60	3.7	29	6.9	4.22	93	1.51	21.6	74	3.23

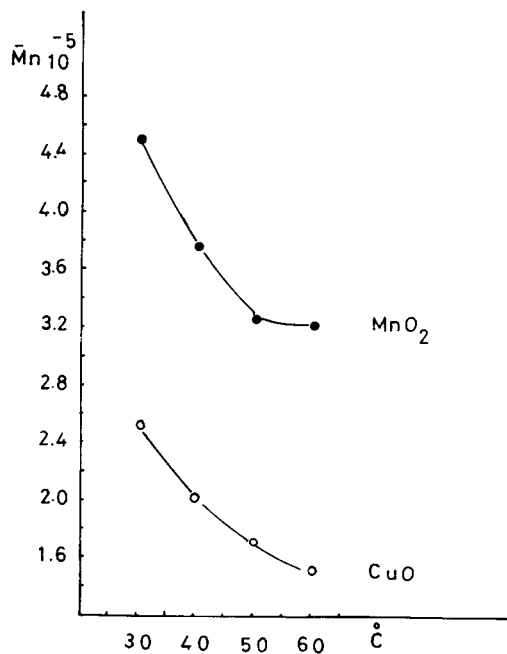


Fig. 4. Effect of temperature on \bar{M}_n .

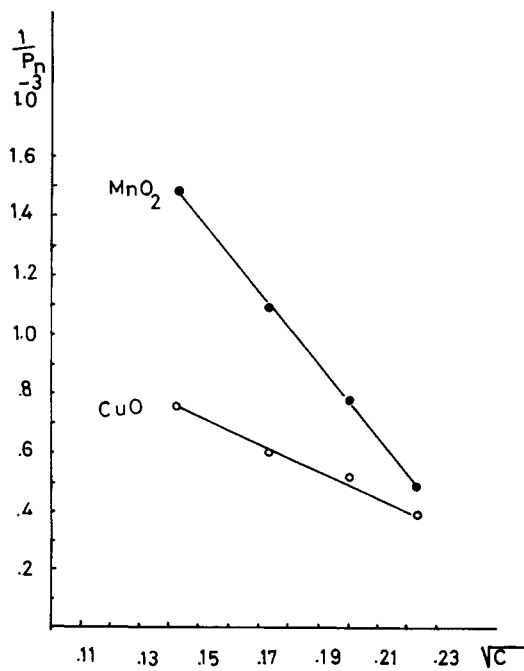
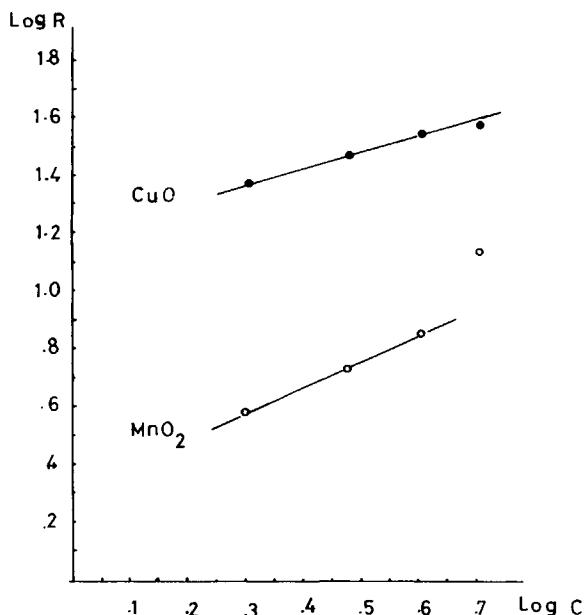


Fig. 5. Plot of $1/P_n$ vs. \sqrt{c} .

Fig. 6. Plot of $\log R$ vs. $\log c$.

average molecular weights increased from 0.7×10^5 to 2.4×10^5 and from 1.5×10^5 to 7.1×10^5 when the monomer concentration increased from 0.235 mole/l. water to 1.17 mole/l. water when using cupric oxide and manganese dioxide (10 g/l. water), respectively.

Indeed, the largest part of polymerization takes place in the water layer and on the metal oxide; besides, a smaller part takes place at the interfacial phase between the monomer layer and the water layer, and another small part takes place in the monomer layer.¹² That is why we would like to relate our concentrations to the volume of water.

The polymerization of methyl methacrylate (10 g) in water (100 ml) using sodium bisulfite as initiator (0.05 mole/l.) in presence of some metal oxides (0.9 g) was performed. The effect of temperature on both the rate of polymerization and on the number-average molecular weight of the poly(methyl methacrylate) formed was studied, and the data are given in Table IV and represented in Figures 3 and 4.

In Table IV, the initial rate of polymerization was found to increase from 0.7×10^{-5} mole/(l. sec) to 3.7×10^{-5} mole/(l. sec), 4.2×10^{-5} mole/(l. sec) and 7.2

TABLE V
Polymerization of MMA (9.4 g) in Water (100 ml) Using NaHSO_3 (0.05 mole/l.)
in Absence and in Presence of Cuprous Oxide (1 g)

Atmosphere	Conversion, %, in presence of Cu_2O				Conversion, %, in absence of oxide $\bar{M}_n \times 10^{-4}$		
	30 min	60 min	120 min	180 min	120 min	180 min	
Nitrogen	58	88	90.9	91.3	11.5	23	9.51
Air	74	91	91.3	92.1	12.4	32.3	8.64

$\times 10^{-5}$ mole/(l. sec) when the temperature was raised from 30°C to 60°C in absence and in presence of cupric oxide and manganese dioxide (9 g/l.), respectively. The number-average molecular weight was also found to decrease with increase in temperature; it decreased from 2.52×10^5 to 1.51×10^5 and from 4.51×10^5 to 3.23×10^5 when the temperature was raised from 30°C to 60°C in case of cupric oxide and manganese dioxide, respectively.

From all the previous experiments, it is clear that cupric oxide accelerates the polymerization reaction to a greater extent than manganese dioxide; this was assured by calculating the apparent energy of activation (E_a) between 40°C and 50°C. E_a was calculated in the same way described in a previous publication.⁶ It was found to be 0.833 kcal/mole and 4.273 kcal/mole when cupric oxide and manganese dioxide (9 g/l.) were used, respectively. It has also been found that the rate of polymerization is faster in air than in nitrogen under the given conditions. The data are given in Table V.

The data are in accordance with the findings of Yamazaki et al.¹³ who found that the sodium bisulfite-initiated polymerization of methyl methacrylate is inhibited by oxygen in case of low concentrations of bisulfite below 0.01 mole/l.; but when the concentration of bisulfite was higher than 0.03 mole/l., the polymerization reaction was accelerated by oxygen.

The number-average molecular weight of the obtained poly(methyl methacrylate) was found to be somewhat higher in case of nitrogen than in air.

Sodium bisulfite-initiated polymerization of methyl methacrylate reciprocal degree of polymerization, $1/P_n$, of the polymers in benzene solution at 35°C versus the square root of initiator concentration is represented in Figure 5, while the double-logarithmic plot of initial rate of polymerization in mole/(l. sec) versus concentration of NaHSO_3 in mole/l. is represented in Figure 6.

CONCLUSIONS

Both cupric oxide and manganese dioxide can be taken as promoters for the sodium bisulfite-initiated polymerization of methyl methacrylate. Both decreased the apparent energy of activation for the polymerization of MMA in such a system. Air accelerated the polymerization to a larger extent than nitrogen. The number-average molecular weights of the poly(methyl methacrylate) formed in pure nitrogen were found to have somewhat higher values than those formed in air.

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