Polymerization of Methyl Methacrylate in Water in Presence of the Metal Oxides TiO_2 and Cu_2O

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Synopsis

Rates of sodium bisulfite-initiated polymerization of methyl methacrylate in water were determined in absence and in presence of the metal oxides TiO_2 and Cu_2O at 30°, 40°, 50°, and 60°C. Cuprous oxide and titanium dioxide enhanced the rate of polymerization and reduced the molecular weight as compared with the figures obtained in absence of oxide, the effect of the former being more pronounced than the latter. With TiO_2, the rate was increased from 2.3 to 3.2 × 10^{-5}, while with Cu_2O, it was increased to 8.6 × 10^{-5} mole/l./sec, both at concentrations of 9 g/l. water. The apparent energy of activation for the polymerization of methyl methacrylate between 40°C and 50°C was found to be 15.6 kcal/mole in absence of the metal oxides, and 7.6 kcal/mole and 2.8 kcal/mole in presence of titanium dioxide and cuprous oxide, respectively. The number-average molecular weight was found to decrease slightly with the addition of TiO_2 but to decrease greatly when Cu_2O was added.

INTRODUCTION

It was found that the polymerization of methyl methacrylate in water was catalyzed by the presence of many inorganic materials such as sand, calcium sulfite,[1] soda lime glass,[2,3] ferric oxide,[4] and slags.[5] It was also found that eight different active carbon preparations decrease[6] the rate of polymerization of styrene, contrary to what was reported by Hummel[7] who found that active carbon catalyzed the polymerization. In a recent work, it was found that both graphite[8] and silicon[9] in an unstirred system catalyze the polymerization of methyl methacrylate in water to some extent.

The aim of the present work is to study the effect of titanium dioxide and cuprous oxide on the rate of polymerization of methyl methacrylate in water, using sodium bisulfite as initiator, and on the number-average molecular weights obtained, and also to throw more light on the polymerization carried out in a heterogeneous system on solid surfaces.

EXPERIMENTAL

Materials

Methyl methacrylate was prepared by a degradation process of polymer scrap,[10] dried by sodium sulfate, and distilled by using a fractionating column (15 theoretical plates). The fraction boiling at 100–100.5°C was collected.

Methanol and benzene were products of El Nasr Pharmaceutical Chemical Co., ARE; the nonvolatile matter in each did not exceed 0.005%.

Sodium bisulfite was a product of El Nasr Pharmaceutical Chemical Co., ARE, Laboratory Chemical Division, assay SO_2 not less than 60%. Titanium dioxide and cuprous oxide were pure products from VEB LABORCHEMIE APOLDA.

Purification of Solvents

The solvents were reagent-grade chemicals purified by distillation through a fractionating column of about 15 theoretical plates.

Polymer Preparation

The required amount of titanium dioxide or cuprous oxide was put in a 250-ml well-stoppered conical flask followed by the required amounts of initiator, distilled water, and finally the monomer. This order of addition of substance was fixed in all experiments, as this has been proved to affect the yield of the polymer obtained. The conical flask was shaken five turns per 3 sec every half hour. The polymerization was stopped at will by making the reaction medium fairly alkaline with sodium hydroxide solution.[11]

At the end of the polymerization reaction, the mixture was filtered by suction and the precipitate was washed thoroughly with distilled water and methanol, and finally dried at 50°C.

Polymer Precipitation and Purification

A certain amount of the titanium or cuprous oxide polymer composite was treated with a suitable volume of benzene to give approximately 2% polymer solution and left overnight with occasional shaking. The polymer solution was filtered with a sintered glass filter G3. In some cases, it was necessary to use a laboratory centrifuge to settle the particles of the metal oxide, which passed through the sintered glass filter, and then decant the polymer solution. The polymer was then precipitated in methanol and dried at 50°C. The process of dissolution and precipitation was repeated, and the polymer was finally dried at 50°C.

Determination of Intrinsic Viscosity and Average Molecular Weight of Polymers

The intrinsic viscosity $[\eta]$ for each polymer was obtained by the usual method of extrapolation.

The number-average molecular weights $\bar{M}_n$ for the respective polymers were calculated from the corresponding $[\eta]$ values by the use of the following equation:

$$\bar{M}_n = 2.81 \times 10^{-5}[\eta]^{1.32}$$

The viscosity measurements were made in benzene at 35°C.

TABLE I

Number Average Molecular Weights and Polymerization Rates in Absence and in Presence of Metal Oxides

| Metal oxide, g/l. | TiO$_2$ | | | Cu$_2$O | | |
	Rate of Polymerization, mole/l./sec × 10$^{5\,a}$	Conversion, %	$\overline{M}_n$ × 10^{-6}	Initial rate × 10$^{5\,a}$	Conversion, %	$\overline{M}_n$ × 10^{-6}
0	1.3 (1.17)	26	1.14	1.3 (1.17)	26	1.14
3	2.2 (2.00)	29	1.05	33.0 (29.83)	85	0.233
5	2.8 (2.53)	31	1.03	36.0 (32.54)	86	0.220
9	3.6 (3.25)	31	0.95	37.0 (33.44)	87	0.200

[a] Figures in parentheses are rates calculated when total volume is taken into consideration.

RESULTS AND DISCUSSION

Effect of Metal Oxides on Conversion Rate

The effect of small amounts of the metal oxides (TiO$_2$ and Cu$_2$O) on the rate of polymerization of methyl methacrylate (10 g) in water (100 ml) using sodium bisulfite (0–0.05 mole/l.) as initiator over a period of 3 hr at 40°C was studied, and the data are given in Table I and represented in Figure 1.

It is clear from Table I that both the initial and overall rates of polymerization in the presence of cuprous oxide are higher than in those in the presence of titanium dioxide. The effect of the two metal oxides on the average molecular weights obtained after a polymerization time of 3 hr is given in the table.
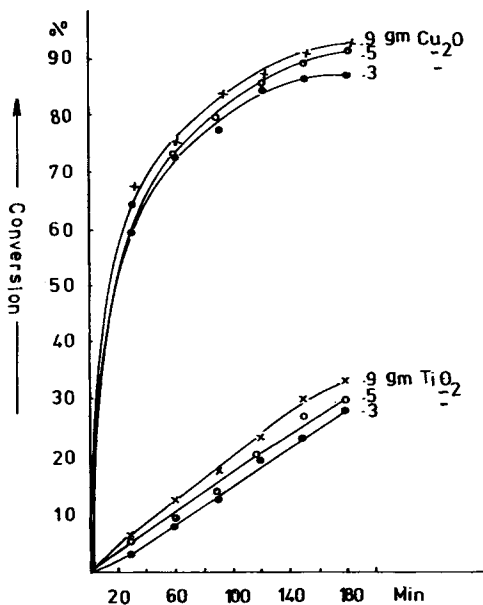

Fig. 1. Effect of metal oxides on rate of polymerization.

TABLE II

Effect of Temperature on Number Average Molecular Weights and Polymerization Rates in Absence and in Presence of Metal Oxides

Temp., °C	Without metal oxide			With TiO$_2$			With Cu$_2$O		
	Rate, mole/l./sec × 10^5 a	Conversion, %	$\bar{M}_n$ × 10^{-5}	Rate, mole/l./sec × 10^5 a	Conversion, %	$\bar{M}_n$ × 10^{-5}	Rate mole/l./sec × 10^4 a	Conversion, %	$\bar{M}_n$ × 10^{-5}
30	0.7 (0.63)	—	—	1.1 (0.99)	20	11.4	3.6 (3.2)	89	2.2
40	2.3 (2.08)	26	11.4	3.3 (2.98)	31	9.45	3.7 (3.3)	91	1.9
50	3.5 (3.16)	25	9.5	5.3 (4.79)	32	6.31	4.0 (3.6)	90	1.6
60	3.8 (3.43)	29	6.9	6.7 (6.06)	20	2.99	4.1 (3.7)	90	1.5

a Figures in parentheses are rates calculated when total volume is taken into consideration.

From the data it is obvious that the number-average molecular weight decreases slightly with addition of TiO$_2$ but decreases greatly when Cu$_2$O was added.

Effect of Temperature

The effect of temperature on both the initial rate of polymerization of methyl methacrylate (10 g) in water (100 ml) using an initiator concentration of 0–0.05 mole/l. and on the number-average molecular weights of the polymers was studied, and the data are given in Table II and represented in Figures 2, 3, and 4.

The number-average molecular weights are determined at the conversion percentages given in the tables at different polymerization times. It is clear
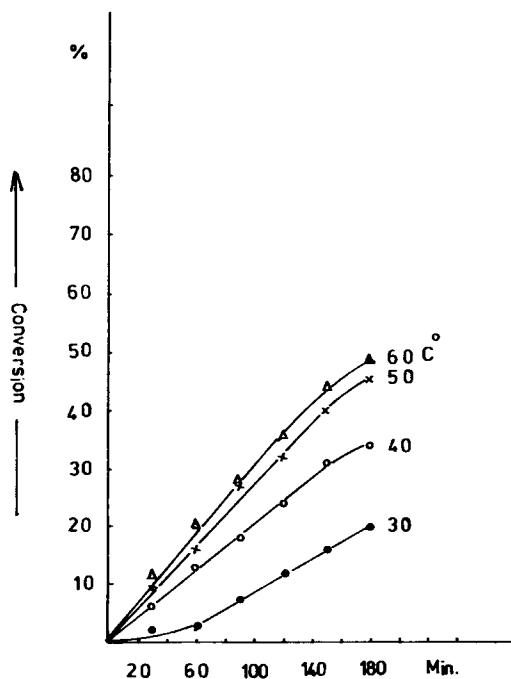

Fig. 2. Effect of temperature on rate of polymerization in presence of TiO$_2$.

that the number-average molecular weight decrease is greater when titanium dioxide is present and more so when cuprous oxide is used.

The effect of conversion percentage on the number-average molecular weights formed under the same condition (MMA, 10 g; H_2O, 100 ml; $NaHSO_3$, 0.05 mole/l.), but polymerized in absence of metal oxides was studied, and the data are given in Table III.
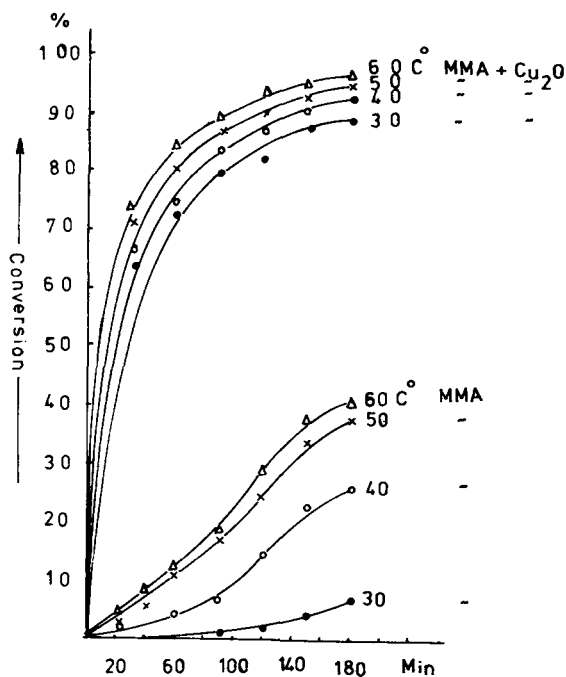

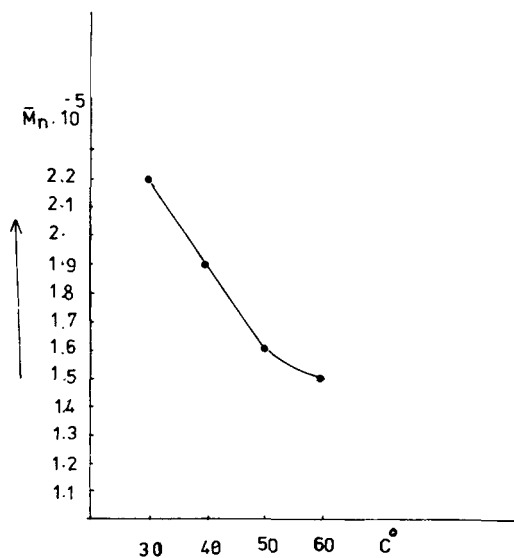Fig. 3. Effect of temperature on rate of polymerization.

Fig. 4. Effect of temperature on $\bar{M}_n$ in case of Cu_2O.

TABLE III
Effect of Conversion on the Obtained Number Average Molecular Weights

Temp., °C	Time, min	Conversion, %	$\overline{M_n} \times 10^{-5}$
30	150	16	10.5
30	180	20	11.4
50	60	16	5.3
50	120	32	6.3

TABLE IV
Effect of Initiator Concentration on Number Average Molecular Weights and
Polymerization Rates

Initiator, mole/l.	With TiO$_2$			With Cu$_2$O		
	Initial rate, mole/l./sec $\times 10^{5\,a}$	Conversion, %	$\overline{M_n} \times 10^{-5}$	Initial rate, mole/l./sec $\times 10^{4\,a}$	Conversion, %	$\overline{M_n} \times 10^{-5}$
0.02	1.0 (0.90)	11	—	3.1 (2.80)	78	0.76
0.03	1.4 (1.26)	14	4.9	3.3 (2.98)	81	1.00
0.04	1.9 (1.72)	22	6.9	3.5 (3.16)	82	1.30
0.05	3.6 (3.25)	34	10.7	5.4 (4.88)	84	2.20
0.05[b]	0.6 (0.54)	26	11.4	— —	—	—

[a] Figures in parentheses are rates calculated when total volume is taken into consideration.
[b] In absence of metal oxides.

It is clear that the number-average molecular weights, obtained at the same conditions of temperature, initiator, and monomer concentrations, increase moderately as the reaction time increases.

Effect of Initiator

The polymerization of methyl methacrylate (10 g) in water (100 ml) at 40°C was carried out using different initiator concentrations in presence of 0.9 g titanium dioxide or cuprous oxide. The initial rate of polymerization was calculated, and the average molecular weights were determined at the conversion percentages given. The data are given in Table IV and represented in Figure 5.

From Table IV, it is clear that the number-average molecular weight increases with increase in initiator concentration; this is in accordance with our previous work on heterogeneous polymerization.[12,13] Also the initial rate of polymerization in presence of cuprous oxide is more than ten times greater than when using TiO$_2$.

Effect of Monomer Amount

The polymerization of different amounts of methyl methacrylate in water (100 ml) using sodium bisulfite as initiator (0.05 mole/l.) at 40°C was carried

out for 3 hr in absence and in presence of TiO_2 and in presence of Cu_2O.

The effect of the addition of small amounts of the metal oxide (1 g) on both the overall rate of polymerization and the number-average molecular weight was studied, and the data are given in Table V.

From Table V it is clear that both the overall rate of polymerization and the number-average molecular weight $\bar{M}_n$ increase with increase in monomer concentration. It is also obvious that values of $\bar{M}_n$ in absence of the metal oxides are highest, while the polymerization rate values are lowest. Using 1 g of the metal oxide resulted in increasing the overall rate of polymerization; the increase in case of cuprous oxide is more than in the case of TiO_2. The increased rates and molecular weights with increase of the monomer amount may be attributed to increased sites of reaction at the monomer–water interface and inside the monomer phase when some water-carried initiator dissolves.

A plot of the relation $1/\bar{P}_n$ versus $\sqrt{C}$ is represented in Figure 6, where $\bar{P}_n$ is the degree of polymerization and C is the initiator concentration.

Also, a plot of log rate (R_p in mole/l./sec) versus log C (Fig. 7) gives a straight line the slope of which determines the catalyst exponent. The slope of the curve in absence of metal oxide is different from that in presence of the metal oxide, assuring a role for the metal oxide in the polymerization process and in the structure of the obtained polymers.

Apparent Energy of Activation

Similar to hemogeneous reactions, the influence of temperature on the rate constant K of a heterogeneous reaction is given by the Arrhenius equation
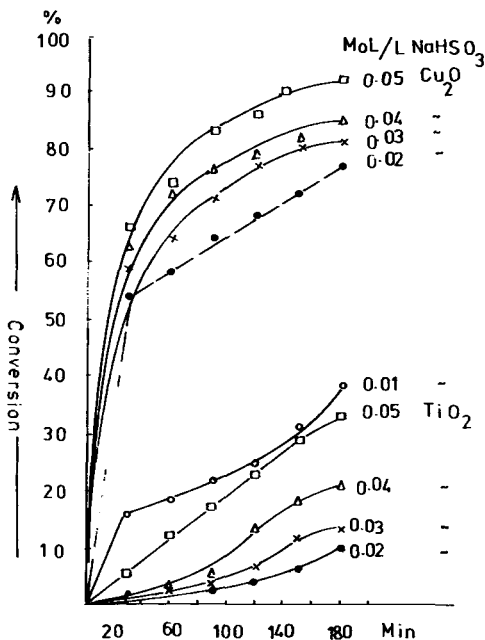

Fig. 5. Effect of initiator on rate of polymerization.

TABLE V
Effect of Monomer Amount on Number Average Molecular
Weights and Overall Rates of Polymerization

MMA, g	Without metal oxide			With TiO$_2$			With Cu$_2$O		
	Overall rate, mole/l./sec × 10$^{5\,a}$	Conversion, %	$\overline{M}_n$ × 10^{-5}	Overall rate, mole/l./sec × 10$^{5\,a}$	Conversion, %	$\overline{M}_n$ × 10^{-5}	Overall rate, mole/l./sec × 10$^{5\,a}$	Conversion, %	$\overline{M}_n$ × 10^{-5}
2.35	1.70 (1.51)	79	2.7	1.86 (1.68)	87	3.8	2.1 (1.9)	96	0.73
4.70	1.87 (1.69)	43	4.6	3.55 (3.20)	82	6.9	4.3 (3.89)	97	1.04
7.05	2.14 (1.93)	33	6.7	4.31 (3.90)	66	9.6	6.2 (5.6)	95	1.46
9.40	2.26 (2.04)	26	11.4	4.34 (3.92)	51	10.6	8.1 (9.3)	93	1.96
11.75	2.32 (2.10)	21	19.0	4.55 (4.11)	42	17.0	10.2 (9.2)	92	2.13

[a] Figures in parentheses are rates calculated when total volume is taken into consideration.

$$\log_{10} \frac{K_2}{K_1} = \frac{E_a}{2.303R} \cdot \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

where E_a is the apparent activation energy, K_1 and K_2 are the velocity constants, T_1 and T_2 are absolute temperatures, and $R = 1.985$ calories.

It is not necessary that the energy required to activate the reactants on the surface is the true activation energy. The latter may be modified by the heats of adsorption of reactants or reactants and products, to give an apparent activation energy which may be quite different from the true one. In a previous work,[4] the apparent activation energy for the polymerization of methyl methacrylate in water between 40° and 50°C was found to be 15.6 kcal/mole, which was also found by Kiyoshi et al.[14]
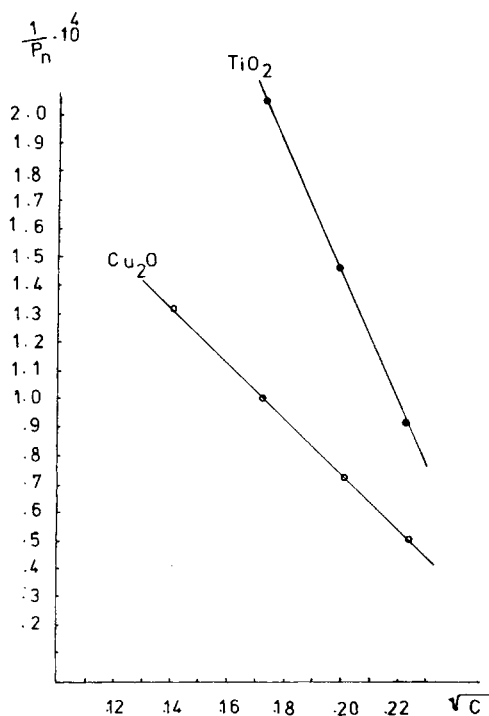

Fig. 6. Plot of $1/\overline{P}_n$ vs. $\sqrt{C}$.

The apparent energy of activation for the polymerization of methyl methacrylate (10 g) in water (100 ml) between 40° and 50°C in presence of 0.9 g TiO_2 or Cu_2O was found to be 4.4 kcal/mole and 0.8 kcal/mole, respectively. Consequently, the presence of titanium dioxide or cuprous oxide leads to a lowering of the net energy required for the activation of methyl methacrylate to be polymerized.

This lowering of the activation energy is brought about by change of the mechanism of the reaction caused by presence and participation of solid surfaces in the polymerization reaction sequence.

Mechanism

The mechanism of initiation and propagation was mentioned in a previous publication.[1] The role played by the metal oxides may be explained by the creation of the active centers as unstable intermediates in the interaction between the oxide and the initiator.

CONCLUSIONS

The metal oxides TiO_2 and Cu_2O increase the rate of polymerization of methyl methacrylate in water and decrease the number-average molecular weight.   They also affect the structure of the obtained polymers.

Cuprous oxide was found to be more effective than titanium dioxide, as the apparent energy of activation was lower in the case of Cu_2O.
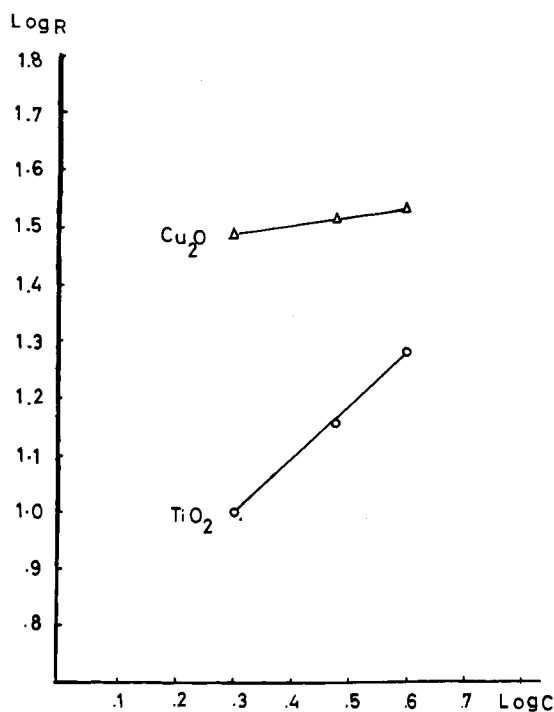

Fig. 7. Plot of log R vs. log C (R = initial rate).   Conversion is related to water volume.

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