

Emulsion Polymerization of Methyl Methacrylate in the Presence of Burnt Mazote Boiler Deposit

A. B. MOUSTAFA, A. S. BADRAN, and S. M. M. SHANDY, *Laboratory of Polymers and Pigments, National Research Centre, Dokki, Cairo, Egypt*

Synopsis

The emulsion polymerization of methyl methacrylate (MMA) using different initiators was carried out in the absence and presence of burnt mazote boiler deposit (BMBD). When sodium persulfate or potassium persulfate was used, the initial rate of polymerization was found to decrease with increase of the burnt mazote boiler deposit concentration but to increase when sodium bisulfite was used as initiator. The initial rate of polymerization was found to be higher in nitrogen atmosphere than in air. The apparent activation energy (E_a) was found to be 12.4×10^4 J/mol and 16.3×10^4 J/mol in the absence and presence of burnt mazote boiler deposit when potassium persulfate was used as initiator and 5.9×10^4 J/mol and 5.1×10^4 J/mol when sodium bisulfite was used as initiator, respectively. The mean average molecular weights for PMMA were found to increase with increase of the burnt mazote boiler deposit when sodium bisulfite was used as initiator.

INTRODUCTION

The emulsifier-free emulsion polymerization of methyl methacrylate was previously studied in the absence and presence of different inorganic substances such as sand¹ metal oxides,² quartz pegmatite,³ lead silicate,⁴ and salts of some metals.⁵ In this piece of work, it is intended to find out if there is any catalytic or retarding effect for the burnt mazote ash deposit on the emulsion polymerization of methyl methacrylate.

EXPERIMENTAL

Methyl methacrylate monomer was a product of Merck-Schuchardt, yield 99%, stabilized with 100 ppm hydroquinone; density 20°/4°C, 0.942–0.944 was washed with a small amount of sodium hydroxide solution (10%). The methyl methacrylate was separated with a separating funnel, dried over anhydrous sodium sulfate, and finally fractionated using a fractionating column of about 15 theoretical plates. The initiators used were analytical grade reagents.

Burnt Mazote Boiler Deposit. The upgraded boiler deposit used was $< 125 \mu$ of the chemical composition (Table I).

The emulsifier used was dodecylbenzene sodium sulfonate obtained from the Egyptian Starch and Yeast Co., Alexandria, purified by being dissolved in ethanol and filtered; the alcohol was then evaporated, and the emulsifier was obtained.

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

TABLE I

Oxide	V ₂ O ₅	Fe ₂ O ₃	Al ₂ O ₃	NiO	SiO ₂	CO ₂	SO ₃	Na ₂ O
%	56.16	15.4	6.5	8.2	3.6	0.32	2.8	6.326

viscosity average molecular weight \bar{M}_v for the respective polymer was calculated from the following equation:

$$[\eta] = 0.94 \times 10^{-4} \bar{M}_v^{0.76} \quad \text{dL/g}$$

All viscosity measurements were made in thiophene free benzene at 25°C.⁶

Emulsion Polymerization of Methyl Methacrylate. The emulsion polymerization of methyl methacrylate was carried out in a 250-mL well-stoppered conical flask, using the chosen concentration of one of the initiators (K₂S₂O₈, Na₂S₂O₈, NaHSO₃) together with 0.5 mL of the emulsifier of concentration (0.08 mol/L) diluted with 45 mL water and methyl methacrylate (4.2 g). The reaction mixture was maintained at the required reaction temperature with an automatically controlled thermostat with mild shaking (10 shakings/10 s · 15 min)⁴ for the definite period of time. The polymerization reaction was stopped at will by the addition of 2% (on the weight of monomer) of hydroquinone. The poly(methyl methacrylate) (PMMA) was then filtered, washed, with distilled water, methanol, and finally dried in an electric oven at 105°C till constant weight.

Polymer Purification. The polymer was dissolved in pure thiophene-free benzene to obtain an approximate 2% polymer solution. The polymer was then precipitated by pouring its benzene solution into a definite amount of methanol and stirring it for a certain period of time. The precipitated polymer was then filtered and finally dried at 105°C in an electric oven till constant weight.

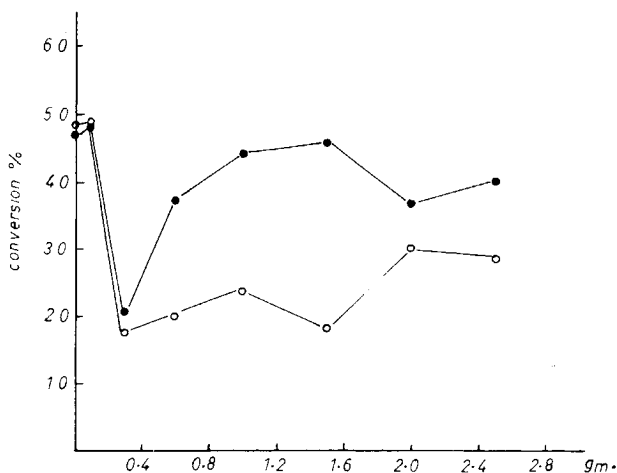


Fig. 1. Effect of BMBD sub. on polymerization: (●) using Na₂S₂O₈ as initiator; (○) using K₂S₂O₈ as initiator.

RESULTS AND DISCUSSION

Effect of BMBD on the Monomer Conversion to Polymer

The effect of BMBD on the conversion % was studied and given in Figure 1, from which it is clear that $\text{Na}_2\text{S}_2\text{O}_8$ was found to be a more effective initiator and that 1.5 g of BMBD had the highest effect under the chosen conditions.

Effect of Different Initiators

The emulsion polymerization of methyl methacrylate (4.2 g) in water (45 mL), using 0.5 mL of the dodecyl benzene sodium sulfonate solution of concentration (0.08 mol/L) as emulsifier and different concentrations of $\text{K}_2\text{S}_2\text{O}_8$ or $\text{Na}_2\text{S}_2\text{O}_8$ as initiator at 40°C for different periods of time, was carried out with mild shaking (10 shakings/10 s · 15 min)⁴ in the absence of BMBD. The data are given in Table II.

From Table II, it is clear that the initial and overall rates of emulsion polymerization of MMA increase with increase of the initiator concentration. It is also clear that the activity of the potassium persulfate as initiator is somewhat higher than sodium persulfate under the same conditions.

The effect of small amounts of burnt mazote boiler deposit (0.1–0.5 g) substance on the rate of emulsifier free emulsion polymerization of methyl methacrylate (4.2 g) in water (45.5 mL) using sodium bisulfite as initiator (0.02 g · mol/L) at 55°C and on the emulsion polymerization of methyl methacrylate using dodecyl benzene sodium sulfonate as emulsifier and potassium persulfate or sodium persulfate (0.02 mol/L) as initiator was studied and the data are given in Table III. From Table III, it is found that when the polymerization reaction was initiated with sodium or potassium persulfate, the initial rate of polymerization decreased with increase of the burnt mazote boiler deposit, while in case of sodium bisulfite the initial

TABLE II
Emulsion Polymerization of MMA Using Potassium Persulfate and Sodium Persulfate at 55°C in the Absence of BMBD

Initiator	Concn (mol/L)	Conversion (%)						Rate of polymerization [(mol/L · s) × 10 ⁴]	
		Time (min)						Initial	Overall
Kine		20	30	40	50	60	70		
$\text{K}_2\text{S}_2\text{O}_8$	0.01	—	12.8	13	18.1	23.7	28.6	0.475	0.55
$\text{Na}_2\text{S}_2\text{O}_8$	0.01	—	10.4	11.1	11.5	15.2	24.3	0.470	0.36
$\text{K}_2\text{S}_2\text{O}_8$	0.02	11.8	24.1	38.5	50.1	61.1	74.1	0.70	1.43
$\text{K}_2\text{S}_2\text{O}_8^a$	0.02 ^a	24	40.8	57.4	64.5	71.9	74.3	1.40	1.68
$\text{Na}_2\text{S}_2\text{O}_8$	0.02	—	19.5	35.8	53.8	64.7	68.9	0.61	1.51
$\text{K}_2\text{S}_2\text{O}_8$	0.03	12.2	35.6	53.6	70.5	84.3	90	0.82	1.97
$\text{Na}_2\text{S}_2\text{O}_8$	0.03	14	29	42.7	58.7	68.5	85.7	0.78	1.60
$\text{K}_2\text{S}_2\text{O}_8$	0.04	19	37.6	54.9	71.6	85.4	91.2	1.08	1.99
$\text{Na}_2\text{S}_2\text{O}_8$	0.04	14.7	29.7	55	69.2	86.9	99.2	0.93	2.03

^a In nitrogen atmosphere.

TABLE III
Effect of Small Concentrations of Burnt Mazote Boiler Deposit Substance on the Rate of Polymerization Using Different Initiators.

Kind of initiator	Initiator concn (mol/L)	Mazote boiler deposit substance (g)	Conversion (%)							Initiator rate $\times 10^4$ (mol/L · s)
			Time (min)							
			10	20	30	40	50	60	70	
$\text{Na}_2\text{S}_2\text{O}_8$	0.02	Nil	—	6.1	18.1	33.7	57.5	59.0	66.8	0.58
NaHSO_3	0.02	Nil	6.0	9.9	16.3	19.4	19.7	26.3	—	0.70
$\text{Na}_2\text{S}_2\text{O}_8$	0.02	0.10	—	2.6	4.5	11.7	31.3	50.5	60.7	0.36
NaHSO_3	0.02	0.10	15.2	33.2	61	80.0	93.6	93.7	—	1.56
$\text{Na}_2\text{S}_2\text{O}_8$	0.02	0.30	—	2.3	4.1	6.0	8.5	8.9	10.2	0.25
NaHSO_3	0.02	0.30	15.4	41.9	61.9	87.9	94.0	94.5	—	2.00
$\text{Na}_2\text{S}_2\text{O}_8$	0.02	0.50	—	1.7	3	3.8	7.0	8.8	9.8	0.19
NaHSO_3	0.02	0.50	21.8	47.6	68.3	91.0	96.2	98.1	—	3.50
$\text{K}_2\text{S}_2\text{O}_8$	0.02	0.50	—	—	1.2	2.7	3.2	4.8	7.4	0.17

TABLE IV
Apparent Activation Energy E_a for the Emulsifier-Free Emulsion Polymerization of MMA (4.2 g) in Water (45.5 mL)^a

Temp (°C)	Burnt mazote deposit (g)	Conversion (%)						Initial rate $\times 10^4$ (mol/L · s)	$E_a \times 10^{-4}$ (J/mol)
		Time (min)							
		10	20	30	40	50	60		
50	Nil	—	5.2	6.1	13.0	14.3	15.0	0.41	5.9
55	Nil	6	9.9	16.3	19.4	19.7	26.3	0.56	
60	Nil	6.3	12.1	16.8	19.6	20.5	28.0	0.84	
50	0.10	11.6	23.5	28.4	67.2	73.1	—	1.27	5.1
55	0.10	15.2	33.2	61.0	80.0	93.6	93.7	1.56	
60	0.10	17.5	42.2	63.5	83.0	95.0	—	2.33	

^a Using NaHSO_3 0.01 g · mol/L as initiator in the absence and presence of 0.1 g BMBD substance.

rate was found to increase with increase of BMBD substance; this could be attributed to the different catalytic effect for both initiators under the taken reaction conditions.

Determination of Apparent Activation Energy E_a

The apparent activation energy (E_a) for the emulsion polymerization of methyl methacrylate (4.2 g) in water (45 mL) using NaHSO_3 (0.02 mol/L) as initiator in the case of emulsifier-free emulsion polymerization and $\text{K}_2\text{S}_2\text{O}_8$ (0.02 mol/L) as initiator using 0.5 mL dodecyl benzene sodium sulfonate (0.08 mol/L) as emulsifier in the absence and presence of 0.1 g BMBD at 50°C, 55°C, and 60°C. The data are given in Tables IV and V and represented in Figure 2. From Table IV, it is seen that the apparent activation energy E_a decreased from 5.9×10^4 J/mol to 5.1×10^4 J/mol among 50°C, 55°C, and 60°C when 0.1 g burnt mazote boiler deposit was used in the reaction mixture taken when NaHSO_3 was used as initiator, and from Table V, the apparent activation energy was found to increase from 12.4×10^4

TABLE V
Apparent Activation Energy (E_a) for the Emulsion Polymerization of MMA (4.2 g) in Water (45.5 mL)^a

Temp (°C)	BMBD (g)	Conversion (%)						Initial rate $\times 10^4$ (mol/L · s)	$E_a \times 10^{-4}$ (J/mol)
		Time (min)							
		20	30	40	50	60	70		
50	Nil	2.4	9.2	11.5	18.9	29.4	42.1	0.40	29.7
55	Nil	11.8	24.1	38.5	50.1	61.1	74.1	0.82	
60	Nil	30.0	48.0	62.0	70.0	73.0	76.7	1.87	
50	0.10	2.2	6.3	7.1	7.7	8.3	9.3	0.21	39.0
55	0.10	6.1	10.1	15.8	27.3	43.1	63.4	0.47	
60	0.10	21.2	40.9	48.3	67.7	71.5	76.0	1.40	

^a Using $\text{K}_2\text{S}_2\text{O}_8$ (0.02 g · mol/L) as initiator in the absence and presence of burnt mazote boiler deposit (0.1 g).

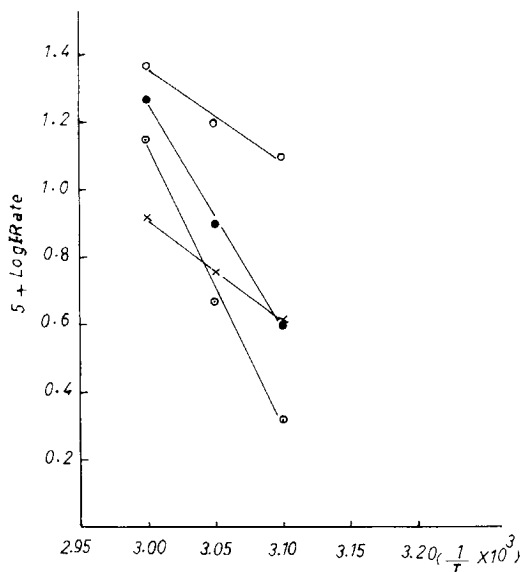


Fig. 2. $\log I$ rate vs. $1/T$: (O) in the presence of 0.10 g BMBD sub. using NaHSO_3 as initiator; (x) in the absence of BMBD sub. using NaHSO_3 as initiator; (●) in the absence of BMBD sub. using $\text{K}_2\text{S}_2\text{O}_8$ as initiator; (⊙) in the presence of 0.10 g BMBD sub. using $\text{K}_2\text{S}_2\text{O}_8$ as initiator.

J/mol to 16.3×10^4 J/mol when 0.1 BMBD was added to the reaction mixture and the polymerization reaction was initiated with $\text{K}_2\text{S}_2\text{O}_8$ among 50°C, 55°C, and 60°C.

Effect of Emulsifier

The emulsion polymerization of MMA (4.2 g) in water (45 mL) using 0.5 mL of the dodecylbenzene sodium sulfonate in different concentrations 0.01, 0.05, and 0.08 mol/L as emulsifier using potassium or sodium persulfate (0.02 mol/L) as initiator was carried out for different periods of time in the absence of BMBD with mild shaking (10 shakings/10 s · 15 min). The data are represented in Figure 3, and the initial rate was found to increase from 6 to 6.5 to 7×10^{-5} mol/L · s and from 5 to 5.8 to 6.4×10^{-5} mol/L · s when potassium persulfate and sodium persulfate (0.02 mol/L) were used as initiator, respectively, when the emulsifier concentration was increased from 0.01 to 0.05 and to 0.08 mol/L, respectively.

The effect of burnt mazote boiler deposit substance on the obtained viscosity average molecular weights was studied by polymerizing MMA (4.2 g) in water (45.5 mL) using NaHSO_3 (0.02 mol/L) as initiator at 55°C for a period of 1 h with mild shaking (10 shakings/10 s · 15 min) in the absence and presence of different amounts of BMBD and the viscosity average molecular weights for the obtained polymers were determined; the data are given in Table VI, where it is found that the obtained viscosity average molecular weights were found to increase with increase of the burnt mazote boiler deposit substance; this indicates that the number of radicals formed decrease with increase of burnt mazote boiler deposit substance.

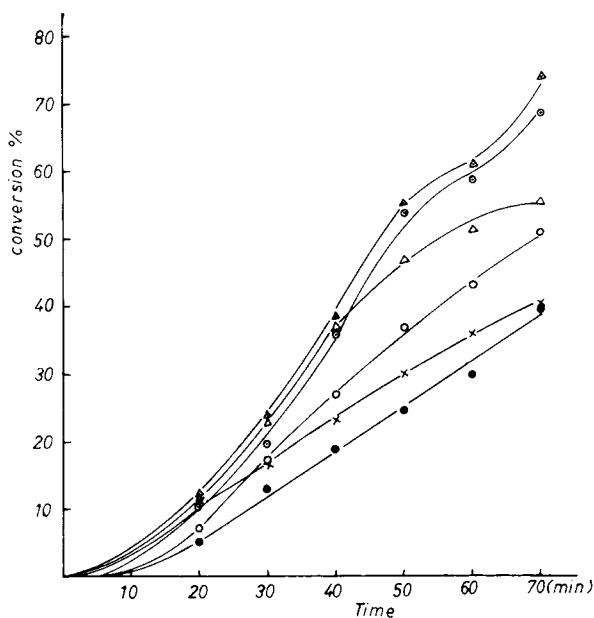


Fig. 3. Effect of emulsifier concentration: (Δ) emulsifier (0.08 mol/L) using $K_2S_2O_8$ as initiator; (\triangle) emulsifier (0.05 mol/L) using $K_2S_2O_8$ as initiator; (\times) emulsifier (0.01 mol/L) using $K_2S_2O_8$ as initiator; (\odot) emulsifier (0.08 mol/L) using $Na_2S_2O_8$ as initiator; (\circ) emulsifier (0.05 mol/L) using $Na_2S_2O_8$ as initiator; (\bullet) emulsifier (0.01 mol/L) using $Na_2S_2O_8$ as initiator.

Kinetics of Polymerization

The results of kinetic studies of the emulsion polymerization of methylmethacrylate are presented in Figure 4. The polymerization starts usually immediately with the addition of the initiator, and the rate curves do not follow the usual course of steady state kinetics. To avoid complication, the initial slopes of the conversion time curves have been taken to determine the initial rate of polymerization (I rate):

TABLE VI
Effect of Burnt Mazote Boiler Deposit on Viscosity Average Molecular Weights Using $NaHSO_3$ or $Na_2S_2O_8$ (0.02 g · mol/L)^a

BMBD wt (g)	Initiator ($\bar{M}_v \times 10^{-5}$)	
	$NaHSO_3$	$Na_2S_2O_8$
Nil	2.96	—
0.5	3.14	1.53
1.0	3.53	1.73
2.0	5.00	1.96
3.0	5.71	—
4.0	6.80	—

^a The authors wish to thank M.Sc. M. M. Momtaz Elsayed Nasr assistant teacher at the NRC for delivering the upgraded burnt mazote boiler deposit sample.

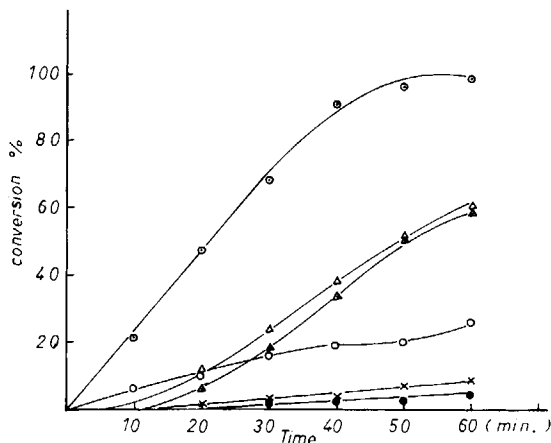


Fig. 4. Conversion time curves: (×) initiator $\text{Na}_2\text{S}_2\text{O}_8$ (0.02 mol/L) + 0.5 g BMBD sub.; (●) initiator $\text{K}_2\text{S}_2\text{O}_8$ (0.02 mol/L) + 0.5 g BMBD sub.; (⊙) initiator NaHSO_3 (0.02 mol/L) + 0.5 g BMBD sub.; (○) initiator NaHSO_3 without BMBD sub.; (△) initiator $\text{Na}_2\text{S}_2\text{O}_8$ without BMBD sub.; (△) initiator $\text{K}_2\text{S}_2\text{O}_8$ without BMBD sub.

$$\text{I rate} = -\frac{d(M)}{dt}$$

$$= \frac{\text{wt polymer} \times 1000}{\text{mol wt monomer} \times \text{reaction mixture vol (mL)} \times t \text{ (s)}}$$

where (M) is the monomer concentration (mol/L) and t is the time (s). A plot of \log rate (mol/L · s) vs. \log (C) gives a straight line (Fig. 5). The slope of this straight line was found to be 0.5 with respect to sodium persulfate and 0.6 with respect to potassium persulfate. The conversion time curves obtained with sodium bisulfite have a quite different shape than those obtained with sodium or potassium persulfate due to the different mech-

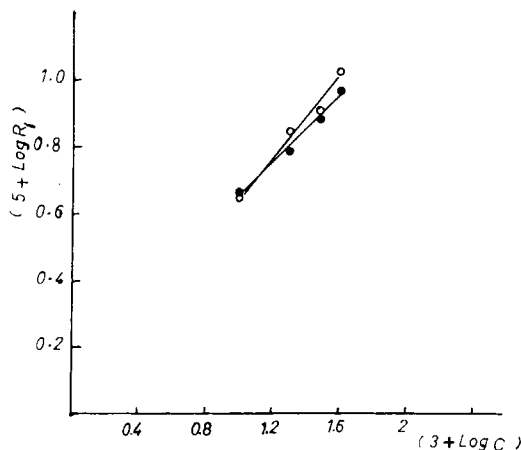
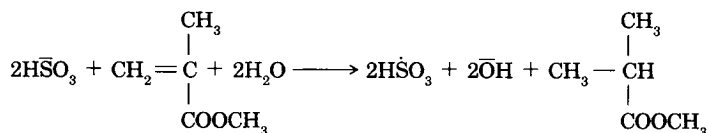


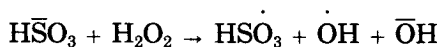
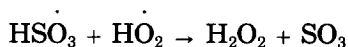
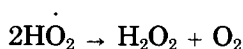
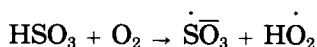
Fig. 5. \log I rate vs. \log C (initiator): (○) using $\text{K}_2\text{S}_2\text{O}_8$ as initiator; (●) using $\text{Na}_2\text{S}_2\text{O}_8$ as initiator.

anisms by which the radicals responsible for the polymerization processes are formed.

The formation of radicals can be expressed by the following equations:



The oxygen present in the system forms a redox pair with bisulfite and generates hydroxyl radicals according to the scheme suggested by Dainton⁸:



Actually OH end groups have been detected in polymers initiated by the bisulfite/O₂ redox system. At high bisulfite concentrations traces of oxygen present in the system become insignificant. The hydrolysis of bisulfite radicals can be expressed as follows: $\text{HSO}_3^\cdot + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 + \text{OH}^\cdot$. This could explain the occurrence of OH end groups.

At high bisulfite concentration such a reaction is practically absent. Mukherjee⁸ assumes that the consumption of bisulfite radicals is so fast that such side reactions do not occur.

With respect to persulfates the radicals formation can be expressed in the following way: $\text{S}_2\text{O}_8^{2-} \rightarrow 2 \text{SO}_4^{\cdot -}$

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