

Characterization of Some Poly(methyl Methacrylate)s Prepared by Emulsion Polymerization in the Presence of Burnt Mazot Boiler Deposit (BMBD)

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Synopsis

The emulsion polymerization of MMA was studied in water using potassium persulfate as initiator and dodocyl benzene sodium sulfonate as emulsifying agent in the absence and presence of burnt mazote boiler deposit (BMBD). The BMBD has a catalytic effect on the polymerization reaction; its effect on the mean average molecular weights of the obtained polymers was also examined by viscosity measurements. The molecular weight distribution was obtained by thin layer chromatographic analysis. The polydispersity for the obtained polymers was wider when prepared in the presence of BMBD. The apparent activation energy among 65, 75, and 85°C for this system was 13.2×10^4 J/mol and 9.2×10^4 J/mol when the polymerization is carried out in the absence and presence of 0.1 g BMBD/20 mL of the reaction mixture, respectively. The suitable mobile phase was ethylacetate or dimethylformamide as single eluent system. In case of binary eluent systems the mobile phase was benzene + methanol (1:1.4 by volume).

INTRODUCTION

It was previously reported that the aqueous polymerization of methyl-methacrylate initiated with sulfur dioxide or sodium bisulfite was catalyzed by natural sand.^{1,2} The catalytic effect depended on the percentage of iron in the sand. The different metal oxides also had a catalytic effect varying from ineffective³ to moderate⁴ to high.^{5,6} Separation of polymeric substances on a molecular weight basis has been studied intensively because of its importance in polymer chemistry for practical as well as academic purposes. All of the available fractionation methods in chromatographic technique belong, from the viewpoint of instrumental classification, to the category of column chromatography. While that depending on the separation mechanism may be classified into three categories, based on phase separation (Baker-Williams method⁷), adsorption (Mark-Saito method⁸), and molecular sieving (gel permeation chromatography, GPC⁹).

TLC can be applied to the fractionation of homopolymers according to their molecular weight.¹⁰⁻¹³ On the other hand, the separation by molecular weight could be attained dominantly through phase separation phenomena that occurs on chromatoplate.^{12,13}

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This paper studies the catalytic effect of the BMBD on the emulsion polymerization of MMA initiated by $K_2S_2O_8$ with continuous stirring (200 rpm) in nitrogen atmosphere and the effect of these additives on the viscosity average molecular weights. Thin layer chromatography for the obtained polymer samples prepared in the presence and absence of BMBD are also studied.

EXPERIMENTAL

Materials

Methyl methacrylate monomer was a product of Merck-Schuchardt (yield 99%), stabilized with 100 ppm hydroquinone, specific gravity $20^\circ/4^\circ\text{C}$, 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 fraction boiling at 100–100.5°C was collected and used. $K_2S_2O_8$ was a product of a Prolabo Chemical Co. Benzene (thiophene-free) and methanol were products of El-Nasr Pharmaceutical Chemical Co. (ARE). The nonvolatile matter did not exceed 0.005%. Dodecyl benzene sodium sulfonate was a product of Starch and Yeast Co. at Alexandria, Egypt. The silica gel type (G 60) which contains gypsum was used as a stationary phase in TLC experiments.

Burnt Mazot Boiler Deposit (BMBD)

Table I shows the chemical analysis of the main constituents of up-graded burnt mazote boiler deposit (BMBD).

Emulsion Polymerization of Methyl Methacrylate

The polymerization was carried out in a three necked Q.F. flask (100 mL) equipped with a stirrer, reflux condenser, and thermometer. The calculated amount of $K_2S_2O_8$ was dissolved at room temperature in 15 mL water containing the emulsifying agent (1%). The monomer quantity was introduced under nitrogen atmosphere, the polymerization system was then put in an automatically controlled water bath at the required temperature during continuous stirring (200 rpm). The reaction was stopped by adding hydroquinone (2% on the monomer weight) and cooling in a cooling mixture. Methanol, 60 mL, was added and the polymer was filtered, washed with distilled water until free from the emulsifier and finally with methanol, and dried in an electric oven till constant weight at 105°C. The weight of the polymer was then determined.

TABLE I
Chemical Analysis of BMBD

Oxide	V_2O_5	Fe_2O_3	Al_2O_3	NiO	SiO_2	CO_2	SO_3	Na_2O
(%)	56.16	15.40	6.50	8.20	3.60	0.32	2.80	6.33

Determination of Intrinsic Viscosity and Average Molecular Weight

The polymer was dissolved in benzene (thiophene free), filtered, and precipitated in methanol and finally dried in an electric oven at 105°C. The intrinsic viscosity $[\eta]$ for each polymer was determined by the usual method of extrapolation. The mean average molecular weight \overline{M}_v for the respective polymers was calculated from the following equation:

$$[\eta] = 0.94 \times 10^{-4} \overline{M}_v^{0.76}$$

The viscosity measurements were made in thiophene-free benzene at 25°C.¹⁴

Thin Layer Chromatographic Analysis

We have applied the TLC method for characterization of PMMA obtained by emulsion polymerization in the absence and presence of BMBD. Silica gel type G 60 activated at 110°C was used as the stationary phase. Ethylacetate and dimethylformamide (DMF) were used as the single mobile phase. In case of binary eluent systems we used benzene + methanol (1:1.4 by volume). The position of the polymer samples after development was marked by spraying a 1% methanol solution of iodine on the layer or a 5% $\text{KMnO}_4/\text{H}_2\text{SO}_4$ (8*N*) solution followed by charring at 120°C.

RESULTS AND DISCUSSION

Effect of BMBD

The emulsion polymerization of MMA (4.7 g) in water (15 mL) using potassium persulfate (0.0185 mol/L) as initiator in nitrogen atmosphere using 1% emulsifier concentration with continuous stirring (200 rpm) was carried out. The polymerization was performed in the absence and presence of BMBD at 65°C. The corresponding data are given in Table II. The initial rate of polymerization increased with an increase in BMBD concentration in the reaction medium and decreased with an increase in the particle size.

TABLE II
Polymerization of MMA Using $\text{K}_2\text{S}_2\text{O}_8$ as Initiator in Absence and Presence of BMBD
(Particle Size 125 μm) at 65°C

No.	BMBD (g)	Conversion (%)	Initial rate $\times 10^3$ mol/L.S.	$M_v \times 10^{-5}$ J/mol.	R_f values
1	Nil	80	0.224	1.922	0.57
2	0.1	82	0.783	1.742	0.61
3	0.3	83	0.979	1.536	0.66
4	0.5 ^a	82	1.306	1.378	0.69
5	0.5	90	1.566	1.312	0.67
6	0.7	94	1.958	1.209	0.70

^a Particle size > 210 μm .

^b Using benzene/methanol (1:1.4 by volume) as mobile phase.

It increases from 0.224×10^{-3} to 1.958×10^{-3} mol/L s, when 0.7 g BMBD was used. The viscosity average molecular weights decreased with an increase in BMBD.

Effect of Reaction Temperature

According to the above-mentioned conditions, the emulsion polymerization of MMA was carried out in the absence and presence of 0.1 g BMBD of particle size $125 \mu\text{m}$ at different temperatures for a period of 1 h. The \bar{M}_v values decreased with an increase in the reaction temperature (Fig. 1). The apparent activation energy (E_a) of the polymerization system was calculated between three different temperatures 65, 75, and 85°C in the absence and presence of 0.1 g BMBD and was 13.2×10^4 J/mol and 9.2×10^4 J/mol, respectively.

Effect of Monomer Concentration

The emulsion polymerization of MMA in water using different monomer concentrations was carried out with two different initiator concentrations (0.0185 and 0.0556 mol/L) and temperatures (75 and 95°C) (Table III). Both initial and overall reaction rates increased with an increase in the monomer concentration; the initial rate values were higher than the overall rates. pH changed from 4 to 2 at the end of the reaction.

Thin Layer Chromatographic Analysis

The behavior of the polymer samples of different viscosity average molecular weights, in single solvent and using normal saturation systems at 30°C was as follows:

1. All polymer samples remained at the start line in the solvents: benzene, toluene, xylene, 1,2-dichloroethane, methylenechloride, chloroform, methanol, and ethanol.

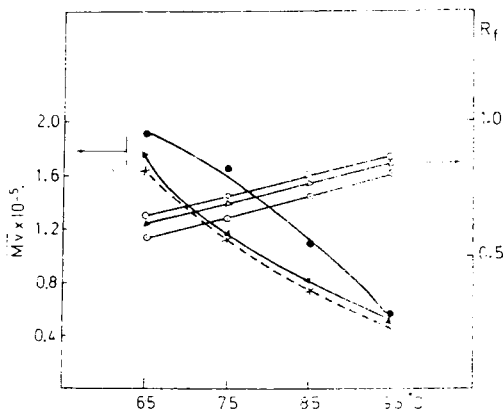


Fig. 1. The effect of temperature on \bar{M}_v and R_f values: (●) \bar{M}_v values in absence of BMBD; (○) R_f values in absence of BMBD; (▲) \bar{M}_v values in presence of 0.1 g BMBD; (△) R_f values in presence of 0.1 g BMBD; (X) \bar{M}_v values in absence of BMBD with initiator concentration (0.0556 mol/L); (○) R_f values in absence of BMBD with initiator concentration (0.0556 mol/L).

TABLE III
Emulsion Polymerization of Different MMA Concentrations Using
K₂S₂O₈ as Initiator at 95°C

Reaction medium			Conversion (%)						Rate of polymerization (mol/L.s) × 10 ⁻³	
			Time (min)						Initial	Overall
Initiator (mol/L)	MMA (mL)	Water (mL)	3	5	10	25	40	60		
0.0185	5	15	45	69	75	78	82	90	11.75	0.59
0.0556	5	15	50	71	80	82	90	95	7.83	0.62
0.0185	5	20	4	14	34	36	44	58	1.04	0.30
0.0556	5	20	6	15	36	56	62	70	1.25	0.37
0.0185	5	25	3	11	29	32	40	52	0.52	0.23
0.0556	5	25	4	13	34	49	59	65	0.58	0.28
0.0185	5	30	2	6	14	29	30	34	0.26	0.13
0.0556	5	30	3	7	24	34	44	50	0.34	0.19

2. All polymer samples moved with the solvent front and gave R_f values (rate of flow) about 1.0 in solvents: acetone, methyl ethyl ketone, acetic acid, tetrahydrofuran (THF), cyclohexanone, and dioxane.

3. The polymer samples gave a good and regular change in R_f values according to change in \bar{M}_v in both ethylacetate and dimethylformamide.

The fractionation of PMMA on thin layer plates in case of single solvents and normal saturation systems at 30°C was the best in the case of both individual solvents such as ethylacetate and dimethylformamide. The graphical representation between the mean average R_f values for both the upper and lower boundaries vs. the viscosity average molecular weights \bar{M}_v shows a linear relationship in the range between 0.561×10^5 and 2.922×10^5 for the following R_f values: (i) in the case of dimethylformamide (DMF) between 0.86 and 0.62; (ii) in the case of ethylacetate between 0.75 and 0.57.

The change in R_f values according to the molecular weight in DMF and ethylacetate (individual solvents) was not sufficient for separation of samples which have more or less approximate values of viscosity average molecular weights. Hence, we investigated a mixed eluent system, one of which is solvent and the other is nonsolvent. The separation in that case is available according to the precipitation chromatography. The following binary systems were studied early for separation of PMMA, chloroform-methanol,¹⁵ acetonitrile-methanol, and ethylacetate-isopropylacetate.¹⁶

The binary eluent used in the present work is a mixture of benzene as a good nonpolar solvent for PMMA and methanol as good polar nonsolvent. Different volume ratios of benzene:methanol was investigated. The best volume ratio which gave a good variation in R_f values according to molecular weights was 1:1.4 benzene to methanol, respectively. The relation between R_f values and viscosity average molecular weights is represented in Figure 2. The change in R_f values lies between 0.81 and 0.45 for \bar{M}_v values of 0.561×10^5 and 2.922×10^5 respectively. This binary system is a good system for comparison between different samples having different \bar{M}_v values. We have developed all the samples of PMMA prepared in the presence and

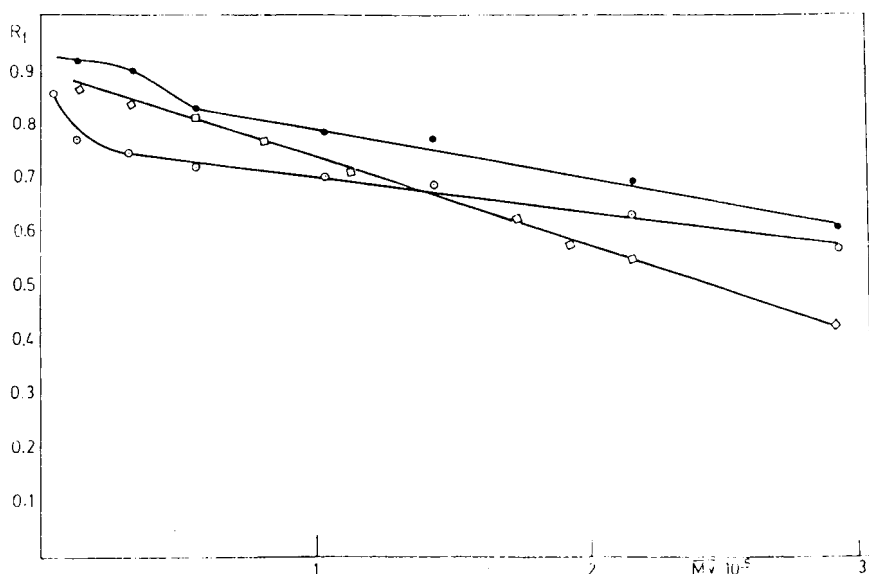


Fig. 2. The correlation between R_f and \bar{M}_v : (●) in DMF at 30°C; (○) in ethylacetate at 30°C; (◇) in binary system benzene/methanol (1:1.4 by volume) at 30°C using normal saturation system.

absence of BMBD in the above-mentioned binary system at 30°C on silica gel layer (0.25 mm thickness) in a normal saturation chamber for three times and average values for R_f was calculated.

The rate of flow (R_f) increased with an increase in the BMBD. The increase of the spot area on the chromatoplate for the investigated polymer samples prepared in the presence of an increasing amount of BMBD indicated a broad molecular weight distribution (Fig. 3 left). The spot area on the chromatoplate for the investigated polymer samples prepared in the presence of equal amounts of BMBD of different particle size have shown an increase in growth with a decrease in particle size and an increase in the R_f values was obtained. The R_f on the chromatoplate for the polymers obtained in the presence of BMBD were higher than those prepared under the same conditions but in the absence of the BMBD. This confirms the viscosity data shown in Figure 1.

The R_f values also increased with an increase in the reaction temperature in the presence of BMBD (0.1 g) (Fig. 3, right). The shape of the spot on the chromatoplate of the polymers prepared in the presence of BMBD is broader than those formed in its absence for the same initiator concentration, denoting a higher polydispersity. The spot area also increases with increasing reaction temperature, and consequently, the polydispersity of the polymer sample increases.

CONCLUSION

The thin layer chromatographic analysis is a good and rapid technique for characterization of polymer samples especially in the determination of molecular weights, and gives an idea about their molecular weight distribution (MWD). The chromatograms obtained from TLC studies on the

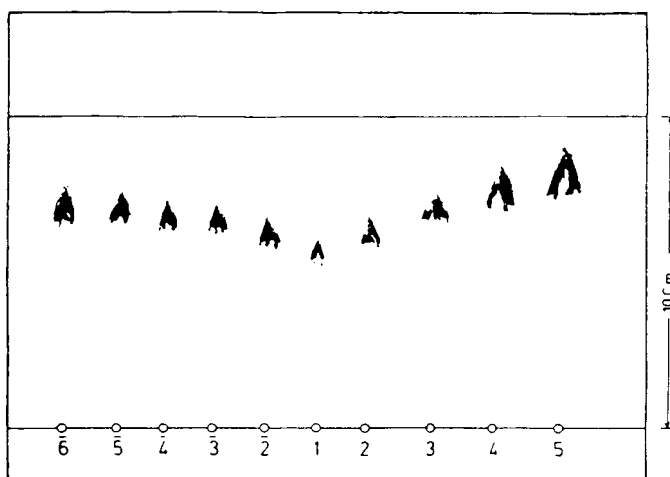


Fig. 3. TLC chromatogram for different PMMA samples prepared in presence and absence of BMBD in benzene/methanol (1:1.4 by volume) at 30°C. Sample no. 1 prepared in absence of BMBD at 65°C. Sample nos. 2–5 (right) prepared in presence of 0.1 g BMBD at 65, 75, 85, and 95°C, respectively. Sample nos. 2–6 (left) prepared at 65°C in presence of 0.1, 0.3, 0.5 (210 μm), 0.5 (125 μm) and 0.7 g BMBD, respectively.

PMMA samples show the effect of the BMBD on both \overline{M}_v and MWD as shown from R_f values and spot shapes of the polymer samples on TLC plates. The spot areas on the chromatoplates and the R_f values for the investigated samples have increased with the decreasing of particle size. The BMBD catalyzed the polymerization of MMA and the mean average molecular weights for the obtained polymers decreased with a rise in the reaction temperature.

References

1. A. B. Moustafa, *Angew. Makromol. Chem.*, **39**, 1 (1974).
2. T. Yamaguchi, H. Tanaka, A. B. Moustafa, et al., *Chemistry and Industry, J. London*, 1974, p. 619.
3. A. B. Moustafa, N. A. Ghanem, and M. A. Diab, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1987 (1975).
4. A. B. Moustafa and A. A. Abd-El-Hakim, *J. Appl. Polym. Sci.*, **21**, 705 (1977).
5. A. B. Moustafa and A. A. Abd-El-Hakim, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 433 (1976).
6. A. B. Moustafa, N. A. Ghanem, and A. A. Abd-El-Hakim, *J. Appl. Polym. Sci.*, **20**, 2643 (1976).
7. C. A. Baker and R. J. P. Williams, *J. Chem. Soc.*, **1956**, 2352.
8. H. Mark and G. Saito, *Monatsh. Chem. J.* **68**, 68 (1936).
9. J. G. Moore, *J. Polym. Sci., A-2*, 835 (1964).
10. B. G. Belenkii and E. S. Gankina, *J. Chromatog.*, Volume 2 **53**, 3 (1970).
11. H. Inagaki, *Bull. Inst. Chem. Res. Kyoto Univ.*, **47**, 196 (1969).
12. F. Kamiyama, H. Matsuda, and H. Inagaki, *Polym. J.*, **1**, 518 (1970).
13. H. Inagaki, F. Kamiyama, and T. Yagi, *Macromolecules*, **4**, 133 (1971).
14. A. L. Goldberg, W. P. Hohenstein, and H. Mark, *J. Polym. Sci.*, **2**, 502 (1947).
15. F. Kamiyama and H. Inagaki, *Bull. Inst. Chem. Res. Kyoto Univ.*, **49**(2), 53 (1971).
16. H. Inagaki and F. Kamiyama, *Macromolecules*, **6**(1), 107 (1973).

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