Characterization of Some Poly(methyl Methacrylate) Prepared by Emulsion Polymerization in Presence of Egyptian Delta Titano Magnetite Ore (EDTMO)

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Synopsis

The emulsion polymerization of methyl methacrylate was studied in water using potassium persulphate as initiator and dedocyl–benzene sodium sulphonate as emulsifying agent at 85°C. The effect of Egyptian delta titano magnetite ore (EDTMO) upon the activation energy and on the mean average molecular weights of the obtained polymers was studied. It was found that the viscosity average molecular weights increase with decrease of reaction temperature and initiator concentration but increase with increase of monomer concentration in the reaction medium. Some of the polymer samples prepared in absence and in presence of some (EDTMO) were separated on tlc plates according to molecular weight in binary mixture, benzene:methanol (1:1.4 by volume) at 30°C. The tlc techniques were performed to give an idea about the molecular weight distribution of the polymer samples obtained.

INTRODUCTION

The emulsion polymerization of methyl methacrylate (MMA) was early studied in the absence and presence of different inorganic substances.[1-4] The effect of these substances on the rate of polymerization, viscosity average molecular weights, and the apparent activation energy of the polymerization process was also studied. A number of investigations have recently been carried out to demonstrate that thin layer chromatograhy (TLC) is capable of a rapid accurate determination of molecular weight distribution of the polymers.[5-7] The separation of atactic and syndiotactic methyl methacrylate polymers has been investigated[8] with TLC technique using a mixture of ethylacetate and isopropylacetate or acetonitrile and methanol binary systems. The separation of PMMA according to molecular weight has been investigated in a mixture of chloroform and methanol (0.71 methanol volume fraction).[9]

In this work we intend to study the emulsion polymerization of MMA in the absence and presence of Egyptian delta titano magnetite ore (EDTMO) using potassium persulphate as initiator. We intend also to have an idea about molecular weight distribution of the obtained polymers using thin layer chromatographic techniques.

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EXPERIMENTAL

Materials

Methyl methacrylate (MMA) 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 sulphate, and finally fractionated using a fractionating column of about 15 theoretical plates. The fraction boiling at 100–100.5°C was used. Potassium persulphate was a product of Prolabo Chemical Co. Benzene thiophene free and methanol were products of El-Nasr pharmaceutical chemical company (ARE), the nonvolatile matter does not exceed 0.005%. Dodecyl benzene sodium sulfonate was a product of Starch and Yeast Company of Alexandria, Egypt. The silica gel type (G 60) which contains gypsum was used as a stationary phase in TLC experiments.

Egyptian Delta Titano Magnetite Ore

The complete analysis of the representative sample is given in Table I.

Purification of Solvents

The solvents were purified by distillation through a fractionating column of about 15 theoretical plates over the suitable drying agent.

Purification of Nitrogen

The nitrogen gas was purified as mentioned in a previous article.[10]

Polymerization Process

The polymerization was carried out in a three-necked flask (100 mL) equipped with a stirrer, reflux condenser, and thermometer. The calculated amount of $K_2S_2O_8$ was dissolved in a 15-mL distilled water solution containing the emulsifying agent (1%). The monomer quantity was introduced under nitrogen atmosphere under continuous stirring of 200 rpm. The polymerization system was then put in an automatically controlled water thermostat at the required temperature. The reaction was stopped at once

TABLE I
Chemical Analysis of Egyptian Delta Magnetite Ore (EDTMO)

Component	(%)	Component	(%)
Fe	56.0	MnO	0.61
FeO	18.6	V_2O_5	0.54
TiO_2	17.8	Na_2O	0.31
SiO_2	1.5	K_2O	0.05
Al_2O_3	1.5	P_2O_5	0.10
Cr_2O_3	0.58	CaO	0.36
S	0.04	—	—

by adding hydroquinone (2% on the weight of monomer) and cooling, 60 mL methanol were added, then the polymer was filtered, washed with distilled water till emulsifier free and finally with methanol, and dried in an electric oven at 105°C till constant weight.

Purification of Polymer

The polymer was dissolved in pure benzene (thiophene free) to obtain approximately a 2% polymer solution, and then filtered to obtain a very clear polymer solution. The polymer was then precipitated by the addition of its solution to a suitable amount of methanol and stirring for a suitable period of time. The precipitated polymer was then filtered and dried in an electric oven at 105°C.

Determination of Intrinsic Viscosity

The intrinsic viscosity [η] for each polymer (at high conversion) was obtained by usual method of extrapolation.The average molecular weights $\overline{M}_v$ for the respective polymers were calculated from the corresponding [η] values by using the following equation:

$$\overline{M}_v = 2.81 \times 10^{-5} [7]^{1.32}$$

The viscosity measurements were made in benzene thiophene-free at 35°C.[11]

Thin Layer Chromatographic Analysis

The fats-free glass plates were washed with distilled water and dried in an oven at 110°C. The stationary phase material for the TLC experiments was Merck silica gel (G 60) which contains gypsum. The Kirschner apparatus was used to adjust the thickness of the stationary phase film to 250 μm. The activation of the plates was then carried out in an oven at 110°C for 3 h. The charged plates with polymer samples were then placed into a chromatographic vessel containing the developing solvent (benzene: methanol 1:1.4 by volume). The used chamber type was normal saturation system at 30°C. The developed plates were removed from the vessel, dried in a hood at room temperature, and heated in an oven at 60–100°C. The visualizing agent was $3N\,H_2SO_4$ followed by charring at 120°C or 5% $KMnO_4$–$8N\,H_2SO_4$ solution.

RESULTS AND DISCUSSION

Effect of Initiator Concentration

The emulsion polymerization of MMA (4.7 g) in water (15 mL) using different concentrations of $K_2S_2O_8$ as initiator was carried out in presence of 0.15 g emulsifier under nitrogen atmosphere for 1 h at 85°C with con-

TABLE II
Emulsion Polymerization of MMA Using Different Initiator Concentration in Presence and in Absence of EDTMO

No.	Initiator concentration (mol/L)	Conversion (%)	Initial rate $\times 10^3$ (mol/Ls)	$\overline{M}_v \times 10^{-5}$	R_f values
1	0.0093	53	0.78	1.432	0.64
2	0.0093[a]	60	1.68	1.109	0.76
3	0.0185	94	3.92	1.085	0.67
4	0.0185[a]	96	4.12	0.773	0.78
5	0.0370	96	7.83	0.703	0.78
6	0.0370[a]	97	9.79	0.567	0.80
7	0.0556	98	15.66	0.573	0.80
8	0.0556[a]	99	19.58	0.504	0.82

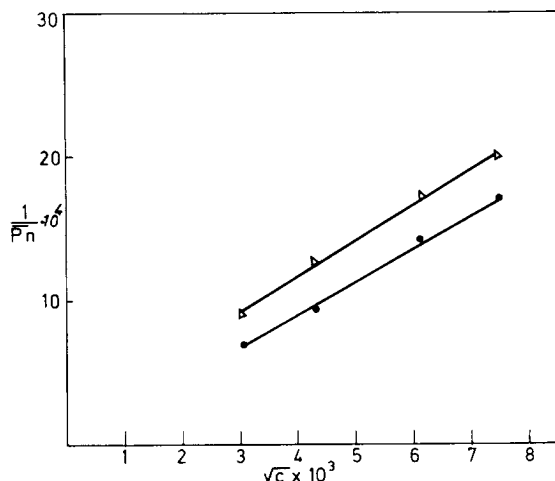[a] In presence of 0.1 g EDTMO–substance.

Fig. 1. $1/\overline{P}_n$ vs. C: ($\triangle$) in presence of 0.1 g EDTMO–substance; ($\bullet$) in absence.

tinuous stirring (200 rpm) and the corresponding data are given in Table II. From Table II it is clear that the mean average molecular weights decrease with increase of the initiator concentration; this is in agreement with the literature. It was also noticed that the EDTMO increases the initial rate of the polymerization reaction and decreases the mean average molecular weights of the obtained polymers.

Plotting $1/\overline{P}_n$ vs. $\sqrt{C}$ (Fig. 1) gave a straight line in addition to what has been previously proved by us,[12] this assures that the polymerization is by a pure radical mechanism. The relation between log C (logarithm of initiator concentration) vs. logarithm of initial rate (log R) is represented in Figure 2; the slope was found to be 1.5 in the absence and presence of EDTMO.

Effect of Substance (EDTMO)

The emulsion polymerization of MMA (4.7 g) in water (15 mL) using $K_2S_2O_8$ (0.0093 mol/L) as initiator was carried out at 65°C with emulsifier
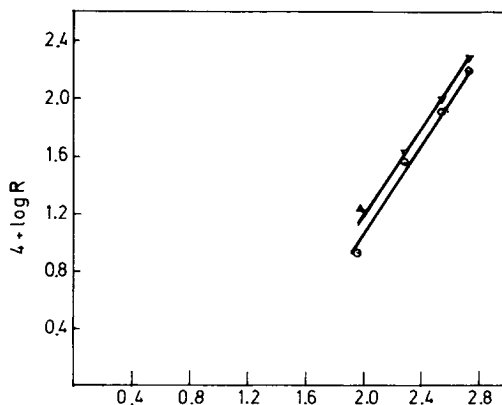

Fig. 2.   log initial rate vs. log C: ($\triangle$) in presence of 0.1 g EDTMO–substance; ($\bigcirc$) in absence.
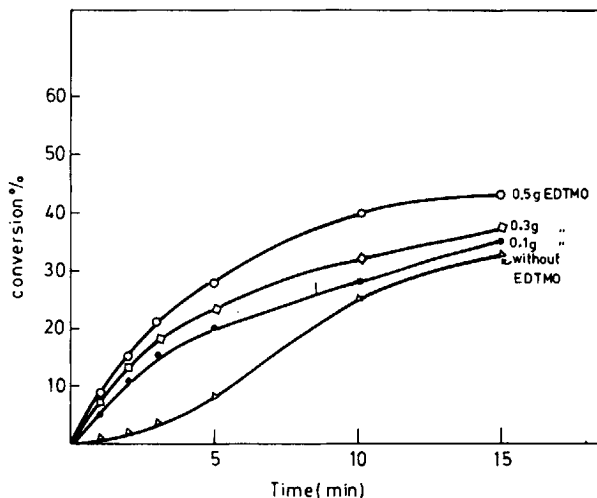
Fig. 3. Conversion–time curves in presence and absence of EDTMO at 65°C.

(0.15 g) in the absence and presence of different amounts of EDTMO–substance with continuous stirring (200 rpm), and the data are represented in Figure 3. From the kinetic curves (conversion % vs. time) and log rate vs. log [initiator], it is clear that the EDTMO–substance catalyzes the polymerization reaction and the rate of polylymerization increases with increase of the substance in the reaction medium.

Effect of Monomer Concentration

The emulsion polymerization of MMA in water using different concentrations of MMA in the presence of $K_2S_2O_8$ (0.0185 mol/L) as initiator and 1% emulsifier for different periods of time at 85°C using mechanical stirring (200 rpm) was carried out, and data are given in Table III. From table III, on one hand, it is clear that the initial rate of the emulsion polymerization of MMA increases with increase of the monomer concentration, and the mean average molecular weights were found to be increased with increase of monomer concentration. On the other hand, it was found that the R_f values increase as the monomer concentration decreases, which confirm the viscosity data.

Effect of Temperature

The emulsion polymerization of MMA (4.7 g) in water (15 mL) using $K_2S_2O_8$ (0.0185 mol/L) as initiator and 0.15 g emulsifier in nitrogen atmosphere in the absence and presence of 0.1 g EDTMO–substance for a period of 1 h with continuous stirring (200 rpm) was carried out at different temperatures, and the data are represented in Figure 4. From Figure 4, it was found that the mean average molecular weights decrease with increase of temperature in both cases, but the R_f values increase with increasing of

TABLE III
Emulsion Polymerization of MMA Using Different Monomer Concentrations

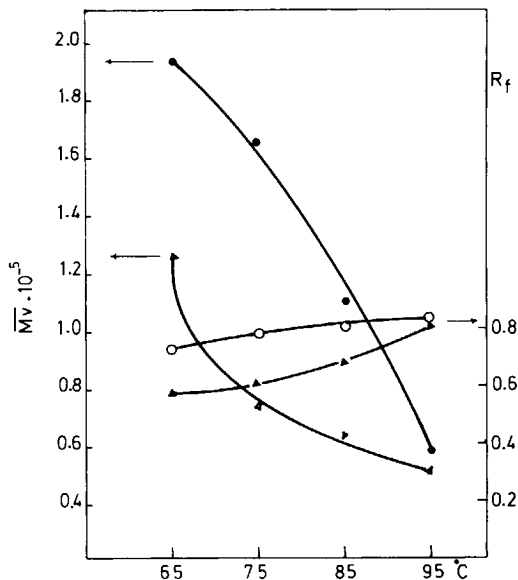| No.	MMA concentration (mol/L)	Conversion (%)	Initial rate $\times 10^3$ (mol/L$\cdot$s)	$\bar{M}_v \times 10^{-5}$	R_f
1	2.35	94	3.92	1.085	0.67
2	1.88	90	1.95	1.037	0.67
3	1.56	88	1.30	0.715	0.78
4	1.34	81	0.87	0.473	.84

Fig. 4. Temperature vs. $\overline{M}_v$ and R_f values: (●) $\overline{M}_v$ in absence of EDTMO–substance; (△) $\overline{M}_v$ in presence of 0.1 g EDTMO–substance; (○) R_f values in presence of EDTMO–substance; (▲) R_f values in absence of EDTMO–substance.

temperature. It was also found that rising the temperature of the reaction has an effect on the molecular weight distribution of the obtained polymers. In both cases (in the absence and presence of EDTMO–substance), it was found that the spot area on the chromatoplates increases with the increase of reaction temperature, but has greater values in the presence of EDTMO. This means generally that the presence of the EDTMO–substance results in wide molecular weight distribution for the obtained polymers (cf. Fig 5).

The Apparent Activation Energy (E_a)

The E_a values of the polymerization system were calculated between three different temperatures 65°C, 75°C, and 85°C. It was found to be 31.5 and 11 cal/mol in the absence and presence of 0.1 g of EDTMO–substance, respectively.

CONCLUSION

In conclusion the thin layer chromatographic analysis is a good and rapid technique for characterization of the polymer samples, especially in the determination of the molecular weight and having an idea about the molecular weight distribution. The TLC studies of the obtained polymers in the presence and absence of EDTMO show that its presence affects both molecular weight and molecular weight distribution (MWD) as shown from the spot shape and R_f values of the polymer samples. (Broader spots and higher R_f values in the presence of EDTMO–substance; cf. Fig. 5).

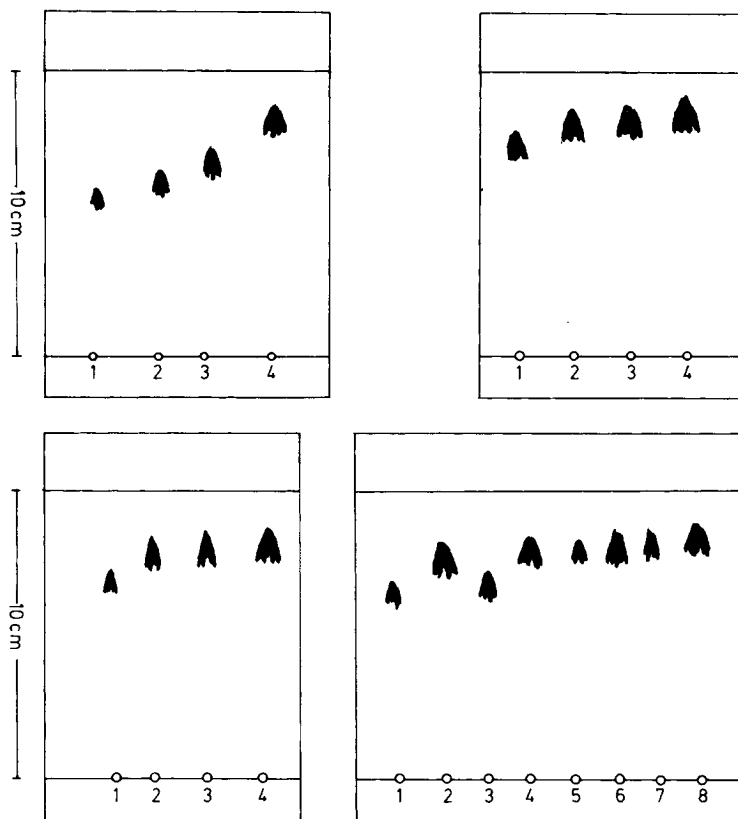The presence of a small amount of EDTMO in the reaction medium lowers

Fig. 5.   TLC chromatograms for different PMMA samples using binary mixture benzene–methanol (1:1.4 by volume) at 30°C. (I) For PMMA samples prepared in absence of EDTMO at 65, 75, 85, and 95°C. (II) For PMMA samples prepared in presence of 0.1 g EDTMO at 65, 75, 85, and 95°C. (III) For PMMA samples prepared in absence (1) and presence (2–4) of concentrations (0.1, 0.3, 0.5) EDTMO. (IV) For PMMA samples represented in Table II.

the molecular weight and activation energy and increases the initial rate of the reaction.

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