Aqueous Polymerization of Methyl Methacrylate Catalyzed by Corundum of Different Particle Sizes

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Synopsis

The aqueous polymerization of MMA in the absence and presence of corundum of different particle sizes was studied, and the effect of corundum on the conversion of monomer to polymer, as well as on the obtained average molecular weights, rate of flow (R_f) values, and activation energy, was also given.

INTRODUCTION

The aqueous polymerization of methyl methacrylate was previously studied in the absence and presence of different inorganic substances.[1-8] In this work we intend to study the effect of particle size of corundum on the initial rate of polymerization, obtained average molecular weights, and flow rate values (R_f).

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) was a product of Merk Schuchardt, purity 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 in a fractionating column of about 15 theoretical plates. The fraction boiling at 100–100.5°C was used. Sodium bisulfate, benzene (thiophene-free), and methanol were products of El-Nasr Pharmaceutical Chemical Company (ARE). The silica gel type (G60) which contains gypsum (13.3%) was used as the stationary phase in the experiments.

Corundum (meshes 600 and 320) was a product of Lawrence Industries (Lawrence Chemical Co. Ltd., U.K.). Complete analysis and specifications of the respresentative samples are given in Table I.

Purification of Solvents

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

Journal of Applied Polymer Science, Vol. 40, 1077–1083 (1990)
 CCC 0021-8995/90/07-81077-07$04.00

TABLE I
Chemical Analysis and Specification of Corundum

Product	Fused aluminum oxide		Typical chemical analysis as oxides	
Grade	600 mesh	320 mesh	Al	96.0% minimum
Color	Brown	Grey	Si	1.10
Mean particle size	9 μm	30 μm	Fe	0.25
Maximum particle size	21 μm	40 μm	Ti	2.55
pH	7.5–8.5		H_2O	0.10
Hardness, Mho	9.0			
Specific gravity	3.8			
Particle shape	Equidimensional			

Polymerization Process

In a well-stoppered conical flask (150-mL capacity), the initiator, inorganic substance (when used), distilled water (100 mL), and finally 4.7 g monomer (methyl methacrylate) were added in nitrogen atmosphere. The order of addition of substances was the same in all the experiments performed. The conical flasks were put in an automatically controlled thermostat at the required temperature. The flasks were shaken (10 shakings for 10 s every 15 min). The reaction was stopped at will by cooling and addition of hydroquinone 2% (on the weight of the monomer) dissolved in cold methanol. The polymer or the mixture of polymer with the inorganic substance was then filtered using a Buchner funnel, washed thoroughly with distilled water, then methanol, dried in an electric oven at 105°C, and then weighed, and the conversion percent was determined.

Determination of Viscosity-Average Molecular Weights

The sample was dissolved in pure benzene (thiophene-free), filtered, and precipitated in a suitable amount of methanol and finally dried in an electric oven at 105°C. The intrinsic viscosity $[\eta]$ for the polymers formed after 3 h was obtained by the usual method of extrapolation.

The viscosity-average molecular weights ($\bar{M}_v$) for the respective polymers were calculated from the corresponding $[\eta]$ values by using the following equation:

$$[\eta] = 0.94 \times 10^{-4} M_v^{0.76}$$

The viscosity measurements were made in thiophene-free benzene at 25°C.[9]

Thin Layer Chromatographic Analysis

The fat-free glass plates were washed with distilled water and dried in an electric oven at 110°C. Silica gel (G60) was used as adsorbent layer with thickness 0.5 mm. The activation of the plates was carried out in an electric oven at 110°C for 3 h. The binary eluent system benzene + methanol (1 : 1.5 by volume) was used as a mobile phase at 25°C using the normal saturation system. The position of the polymer samples after development was marked

by spraying a 5% $KMnO_4/H_2SO_4$ ($8N$) solution followed by charring at 120°C.

RESULTS AND DISCUSSION

Effect of Corundum

The polymerization process was carried out in the presence of two different particle sizes of corundum, namely meshes 320 and 600.

From Table II and Figure 1 it is clear that corundum mesh 600 catalyzes the polymerization reaction by approximately 47% conversion more than in its absence, while corundum mesh 320 was found to catalyze the reaction by about 40% more conversion. This behavior could be attributed to the smaller size of corundum mesh 600, which corresponds to a larger active surface area distributed in the reaction medium. It is also found that increasing the quantity of corundum in the reaction medium decreases the viscosity-average molecular weight and increases the rate of flow R_f values (Fig. 2). The molecular weights of the polymer prepared in the presence of corundum, mesh 320, are much higher than in the presence of corundum mesh 600. The results are summarized in Table II and represented in Figure 3.

From Figures 1–3 it is found that increasing the amounts of corundum over 1 g in the case of mesh 600 and 4 g in the case of mesh 320 resulted in a decrease of conversion percentage, increase in obtained average-molecular weights, and in a decrease in the rate of flow (R_f values).

Effect of Initiator Concentration

The polymerization was carried out in the presence of corundum (mesh 320) using different initiator concentrations. From Table III, it is found that the initial rate of polymerization decreased from 2.1×10^{-5} to 1.3×10^{-5} mol/L s as the initiator concentration increased from 0.2 to 0.3 mol/L, respectively; nearly the same effect was obtained in the case of corundum,

TABLE II
Effect of the Quantity of Corundum Mesh 600 and 320 on the Polymerization of MMA Using 0.1 mol/L as initiator in Nitrogen Atmosphere at 40°C for 3 h

	Corundum mesh 600			Corundum mesh 320		
Wt of Cor.	Conversion (%)	$\bar{M}_v \times 10^{-5}$	R_f	Conversion (%)	$\bar{M}_v \times 10^{-5}$	R_f
0.0	37.8	11.1	0.54	37.8	11.1	0.54
0.5	84.3	6.6	0.70	70.9	10.3	0.59
1.0	85.3	3.8	—	78.5	6.6	—
1.5	86.0	2.2	0.85	80.9	6.6	0.71
2.0	84.4	3.1	—	81.4	5.6	—
2.5	83.1	3.6	0.81	81.7	6.3	0.72
3.0	81.4	3.8	—	82.3	5.9	—
3.5	81.2	5.6	0.74	83.0	4.9	0.76
4.0	80.4	6.3	—	83.6	4.3	—
4.5	80.0	6.3	—	80.3	5.6	—
5.0	77.6	6.6	0.70	79.8	6.3	0.71

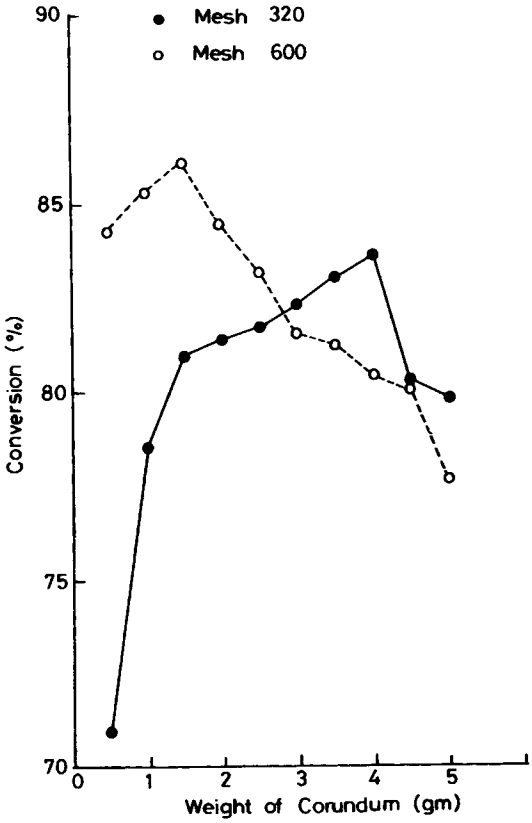

Fig. 1. Conversion percent vs. weight of corundum.

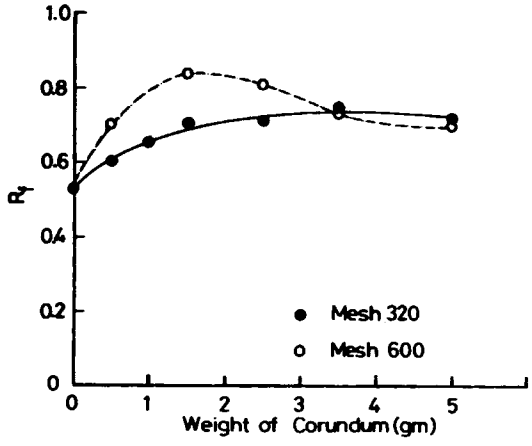

Fig. 2. R_f-values vs. weight of corundum.

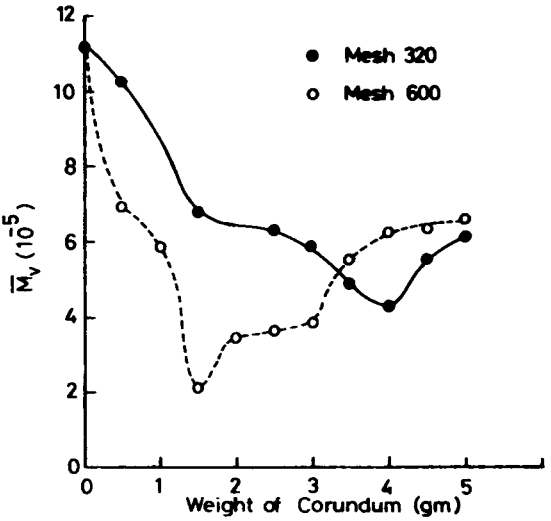

Fig. 3. Viscosity average molecular weight vs. weight of corundum.

mesh 600. This could be attributed to the smaller extent of bisulfite ion formation and consequently less bisulfite radicals formation. For corundum, mesh 320, the average molecular weight decreased from 10.3×10^5 to 8.1×10^5 (g/mol) when the initiator concentration increased from 0.1 to 0.2 mol/L, respectively. Using an initiator concentration more than 0.2 mol/L resulted in an increase of the molecular weights to 9.2×10^5 and 9.9×10^5 when the initiator concentrations were 0.25 and 0.30 mol/L, respectively; this is due to the formation of less radicals and it is in accordance with the previously reported literature.[10]

The effect of initiator concentration in the presence and absence of corundum (meshes 600 and 320) compared with the polymerization carried out in its absence is illustrated in Figure 4. From this figure, it can be seen that by increasing the amount of initiator concentration, the conversion values decreased, but in the presence of corundum (mesh 600) a higher conversion percentage was obtained.

TABLE III
Effect of Initiator Concentration on the Aqueous Polymerization of MMA in the Presence of 0.5 g Corundum at 40°C in Nitrogen Atmosphere

	In the absence of cor.			In the presence of cor. mesh 320			In the presence of cor. mesh 600		
Initiator Concn. (mol/L)	Initial rate of polymerization ($\times 10^5$ mol/L s)	$\bar{M}_v \times 10^{-5}$ (g/mol)	R_f	Initial rate of polymerization ($\times 10^5$ mol/L s)	$\bar{M}_v \times 10^{-5}$ (g/mol)	R_f	Initial rate of polymerization ($\times 10^5$ mol/L s)	$\bar{M}_v \times 10^{-5}$ (g/mol)	R_f
0.1	—	11.1	0.54	1.5	10.3	0.59	—	—	—
0.2	1.1	10.3	0.59	2.1	8.1	0.68	2.1	7.7	0.68
0.25	0.5	12.3	0.55	1.6	9.2	0.62	1.4	8.4	0.67
0.30	0.3	13.1	0.52	1.3	9.9	0.60	1.2	9.6	0.61

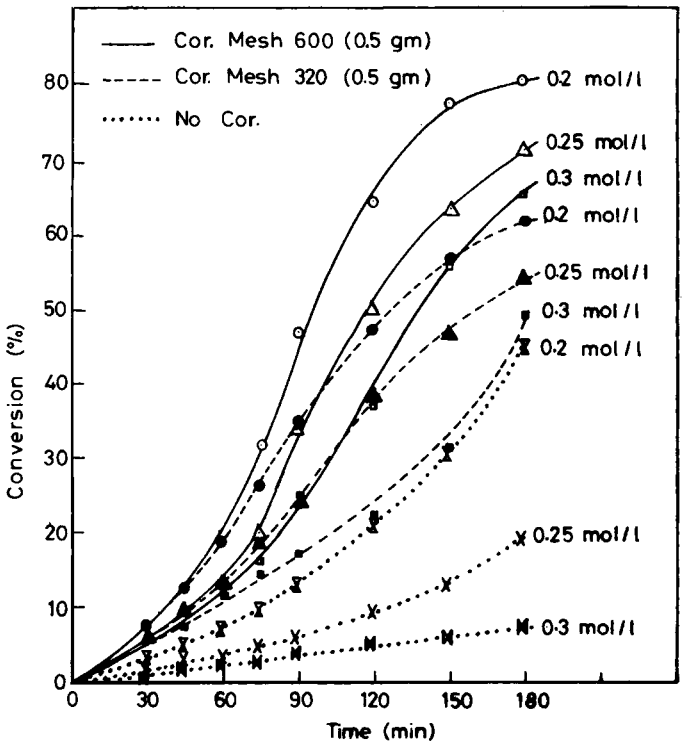

Fig. 4. Effect of initiator concentration on presence and absence of corundum.

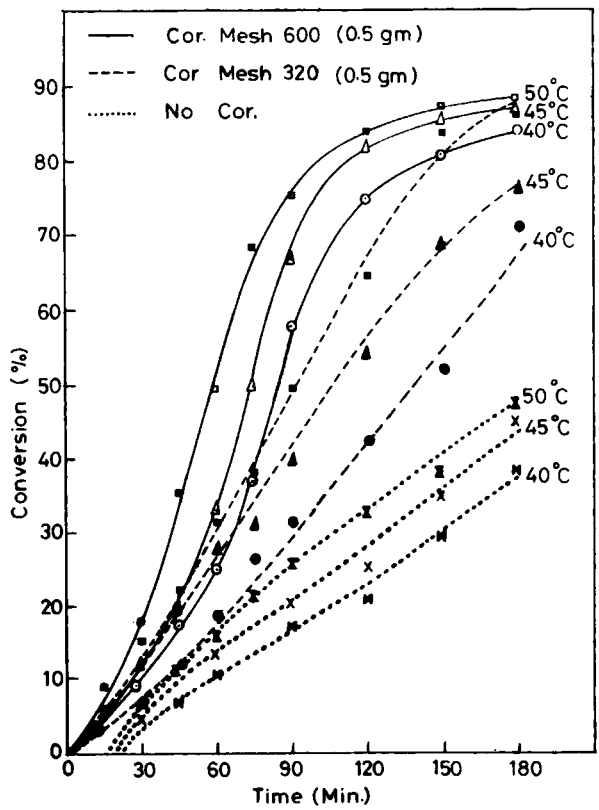

Fig. 5. Effect of temperature on presence and absence of corundum.

Effect of Temperature on the Polymerization Process

The polymerization processes were carried out in the presence of 0.5 g corundum (meshes 320 and 600) at different temperatures namely, 40, 45, and 50°C. The data are represented in Figure 5.

From Figure 5, it is clear that the conversion percentage increases as the temperature increases which is quite logical but the conversion percentage values when using corundum, mesh 320, were lower than the corresponding values obtained when corundum mesh 600 was used, which could be explained through the more active surface area of corundum 600, which is a finer powder.

The apparent energy of activation (E_a) for the polymerization system in the presence of 0.5 g corundum/105 mL reaction mixture between 40 and 50°C was calculated according to a previous publication[5]; it was found to be 3.6×10^4 J/mol in the case of corundum, mesh 320, while it is 1.7×10^4 J/mol when corundum, mesh 600, was used, compared with that carried out in the absence of corundum, which was found to be 4.5×10^4 J/mol.

CONCLUSIONS

The aqueous polymerization of methyl methacrylate was carried out in the absence and presence of corundum of different particle sizes using sodium bisulfite as initiator, producing radicals. Corundum of less particle size (mesh 600) resulted in a higher initial rate of polymerization, lower obtained average molecular weights, a larger rate of flow values (R_f), and a lower energy of activation than in the case of corundum of a larger particle size (mesh 320).

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Received August 7, 1987
Accepted June 9, 1988