

Effect of Modified Calcium Phosphate Surface on the Aqueous Polymerization of Methyl Methacrylate

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Synopsis

The aqueous polymerization of methyl methacrylate was carried out in the absence and in the presence of unmodified and modified calcium phosphate surface with adsorbed stearic acid from stearic acid benzene solution; this was found to accelerate the polymerization process. The acceleration was found to depend on the extent of modification. The apparent activation energy was also found to decrease with surface modification. It was also found that the calcium phosphate surface modified with stearic acid has an effect on the sedimentation rate and sediment volume in organic medium.

INTRODUCTION

A number of publications on the aqueous polymerization of methyl methacrylate in the absence and in the presence of inorganic substances without any surface modification were previously prepared.¹⁻²² We carried out the aqueous polymerization process in the presence of calcium phosphate, a calcium phosphate half-layer, and a monolayer cover modification with stearic acid to find out if there is any effect on the rate and on the apparent activation energy of polymerization.

EXPERIMENTAL

Methyl methacrylate monomer was a product of Merck Schuchardt, yield 99%, stabilized with 100 ppm hydroquinone; $d_{20/24^{\circ}\text{C}}$ 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 with a fractionating column of about 15 theoretical plates. Sodium bisulfite was a product from El-Nasr Pharmaceutical Chemical Co. ARE., assay (SO_2) not less than 60%. Benzene and methanol were analytic-grade reagents. Hydroquinone and stearic acid were from E. Merck (Darmstadt). Calcium phosphate was Abou-Tartour washed concentrate. The surface-active agents used were cetyl trimethyl ammonium bromide, stearic acid from Merck, and Egyptol 85 from Starch & Yeast Co. (Alexandria, Egypt); these are cationic, anionic, and nonionic surface-active agents, respectively. The particle size of the ore gives an idea of its specific surface area, which is an important factor in catalysis. The differential particle size distribution curve of the ore is represented in Fig-

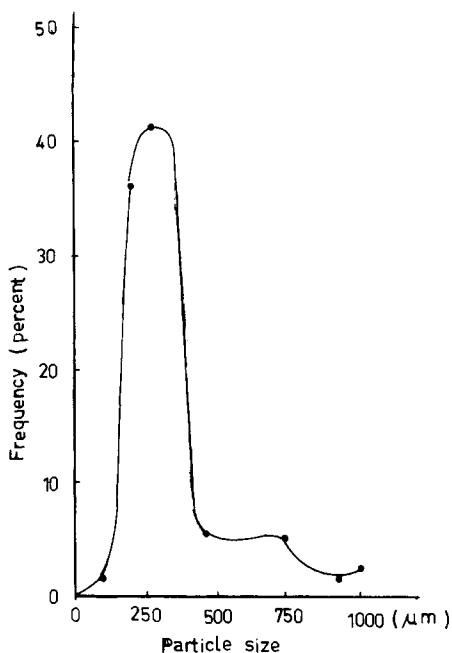


Fig. 1. The particle size—Frequency relation.

ure 1; it was obtained by plotting the mean diameter of the particles in each fraction against its weight percentage. From Figure 1 the largest fraction is of particle size 260 μm .

Calcium phosphate particle size ($-2 + 0.15 \mu\text{m}$) was analyzed, and the data of analysis are given in Table I.

Selection of the Suitable Surface-Active Agent

Calcium phosphate (4 g) is put in each tube of a set of four graduated test tubes closed with quick fitted stoppers: to the first tube was added a cationic (0.05 mol/L) surfactant in benzene, to the second an anionic surfactant, to the third a nonionic surfactant of the same concentration, and to the fourth only benzene (blank), all to 20-ml graduation. The four test tubes were shaken carefully, then allowed to stand (48 h) until equilibrium was attained. The sediment volume was determined. The least sediment volume represents the most efficient surface-active agent.

Determination of the Adsorption Isotherm of Stearic Acid from Benzene on the Surface of Calcium Phosphate

Each of eight graduated test tubes containing calcium phosphate (7 g) was filled with different concentrations of stearic acid solution in benzene (20 ml). The test tubes were left to stand at room temperature for 72 h to

TABLE I
Calcium Phosphate Analysis (%)

P_2O_5	MgO	CaO	SiO_2	Fe_2O_3
31	0.3	50	2	3.5

TABLE II
Surfactant benzene solutions (0.05 mol/L)

	No surfactant	Stearic acid (anionic)	Cetyl trimethyl ammonium bromide	Egyptol BIM 85 (nonionic)
Sedimentation volume $\text{Ca}_3(\text{PO}_4)_2$ (cm^3 per 6 g)	6.5	5.2	6.6	5.5

reach the adsorption equilibrium. The equilibrium concentration of stearic acid in the supernatant benzene layer was determined by titration against alcoholic potassium hydroxide (0.01 *N*) solution. The adsorbed amount of stearic on the calcium phosphate surface was then determined by calculating the difference between the amount of stearic acid added to the benzene at the beginning and the amount of stearic acid determined after equilibrium was attained. The relation between the adsorbed amount of stearic acid (mol/g) and the equilibrium concentration (mol/L) for the various sets of experiments of various concentrations of stearic acid in benzene gives the adsorption isotherm.

Determination of the Sedimentation Rate

A set of six dry test tubes is prepared. In each tube, 1 g calcium phosphate taken from the modified treated samples previously used in the adsorption isotherm determination was added and completed with benzene to 20 mL graduation. The tubes were shaken carefully and left for 48 h to reach equilibrium. Every test tube was shaken for 2 min, and the change of the sedimentation volume with time was determined. The slope of the curve gives the sedimentation rate. The change of the sedimentation rate with the adsorbed amount of stearic acid indicates the relation between the sedimentation rate and the adsorbed amount.

Determination of Sedimentation Volume

Calcium phosphate (6 g) taken from the previously modified treated samples (from the adsorption isotherm), after being dried in an electric oven until constant weight was reached, were put in eight graduated test tubes with ground joints. Benzene was added to the content of each tube to 20-ml graduation. The tubes were then closed with their ground joint stoppers and shaken for 5 min, then allowed to stand. The final sediment volume for every sample was determined.

TABLE III

Initial concentration of stearic acid ($\text{mol} \times$ $10^{-3}/\text{L}$)	0.3	0.6	6	5	30	45	60
Equilibrium concentration ($\text{mol} \times 10^{-3}/\text{L}$)	—	—	0.2	0.65	12	24.2	38.8
Adsorbed amount ($\text{mol} \times$ $10^{-5}/\text{g}$)	0.09	0.17	1.13	3.12	5.1	5.8	6.09

Polymerization Process

Methyl methacrylate (4.7 g) was put in a 250-ml quick-fitted conical flask together with 95 ml water using sodium bisulfite (0.1 g mol/L) as initiator in the absence and in the presence of calcium phosphate, unmodified, half-layer, and monolayer modification. The polymerization process was carried out at different temperatures—40, 45, and 50°C—for different periods of time with mild shaking for 2 min every half-hour. The polymerization was stopped by the addition of hydroquinone (2% of the weight of monomer).

The data for determining the most suitable surface-active agent are given in Table II. From Table II, it is evident that the anionic surfactant is the most suitable modifier for our calcium phosphate sample, as it resulted in obtaining the least sediment volume.

Adsorption Isotherm of Stearic Acid in Benzene on the Surface of $\text{Ca}_3(\text{PO}_4)_2$

Different concentrations of stearic acid in benzene ($0.3\text{--}60 \times 10^{-3}$ mol/L) together with 7 dried calcium phosphate were left to stand at room temperature (25°C) until complete adsorption was attained (72 h). The data of the adsorption isotherm of stearic acid in benzene on the surface of calcium phosphate are given in Table III and represented in Figure 2.

From Figure 2 and Table III it can be seen that the adsorbed amount of stearic acid increases rapidly at the beginning with increase in the equilibrium concentration; then the increase becomes very small, and finally, practically no increase is detected. To obtain the monolayer modification, extrapolation of the steady part of curve²³ to zero equilibrium concentration was carried out. It was found to be 5.4×10^{-5} mol/g. Taking half of this monolayer surface coverage gives the half-layer surface modification (2.7×10^{-5} mol/g).

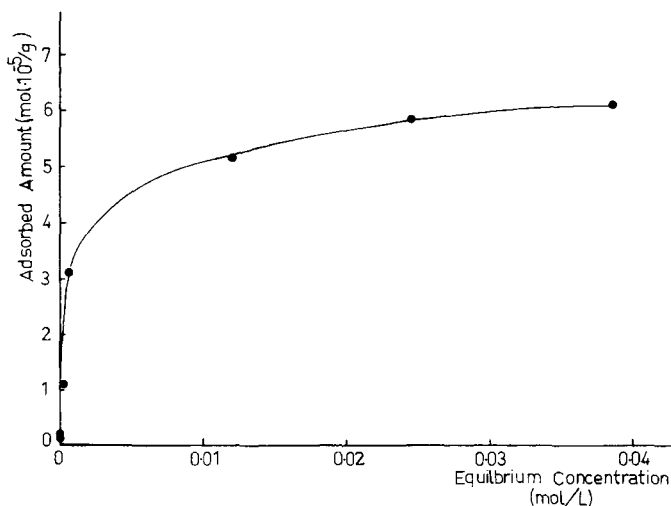


Fig. 2. Adsorbed Amount vs. Equilibrium Concentration.

TABLE IV

Adsorbed amount (mol $\times 10^{-5}$ /g)	—	0.09	1.13	3.12	5.8	6.09
Sedimentation rate (cm ³ /s)	0.2	0.16	0.11	0.07	0.09	0.1

Sedimentation Rate Data

The sedimentation rate for every modified sample was determined and plotted against the adsorbed amount of stearic acid, and the data are given in Table IV and represented in Figure 3.

Sedimentation Volume Data

The test tubes with the material (calcium phosphate modified to a different extent together with benzene) are shaken for 5 min, then allowed to settle to reach equilibrium. The relation between the adsorbed amount and the sediment volume is plotted and represented in Figure 4.

From Figure 4 it is clear that the sediment volume decreases with increase of the adsorbed amount up to a certain value ($5.4 \text{ mol/g} \times 10^{-5}$), followed by no practical change in the sediment volume; this adsorbed amount is the monolayer surface coverage. Comparing this data with the other data obtained from adsorption isotherm, we find that the two results concur with each other. The polymerization process was carried out in the absence and in the presence of calcium phosphate, with and without half-layer modification, and also in the presence of monolayer modification; the data are represented in Figure 5 at 40, 45, and 50°C.

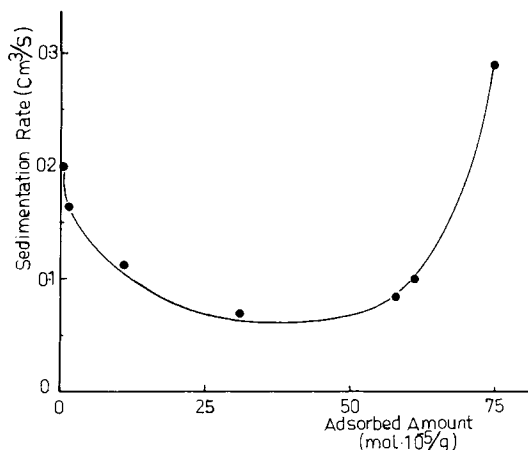


Fig. 3. Sedimentation Rate vs. Adsorbed Amount.

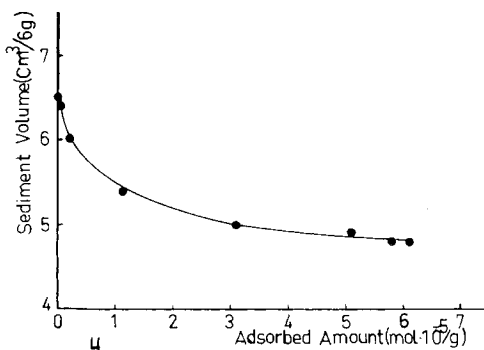
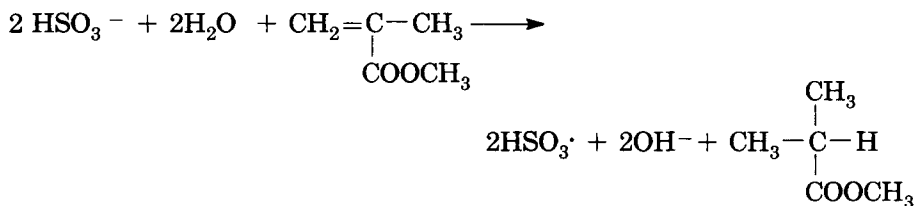


Fig. 4. Sediment Volume vs. Adsorbed Amount.

Mechanism and Kinetics of Polymerization

Radical formation:



Initiation

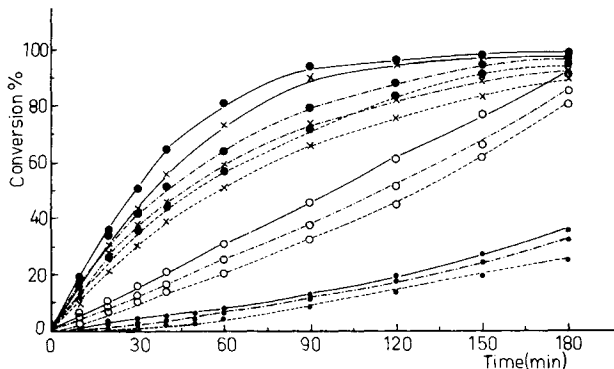
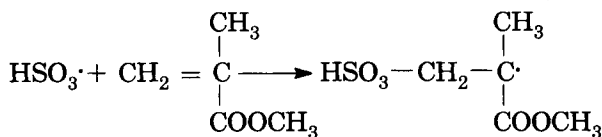
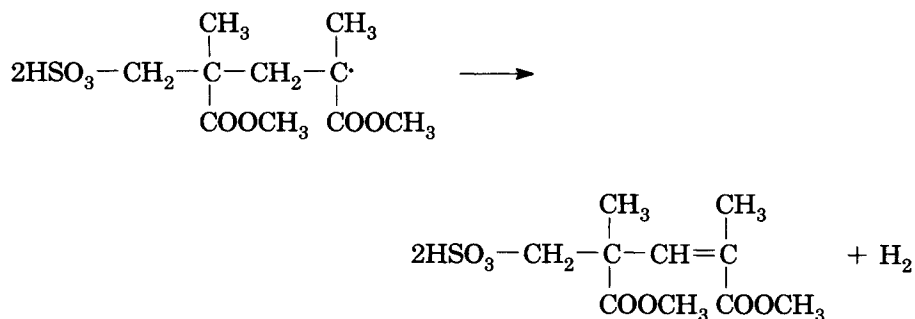
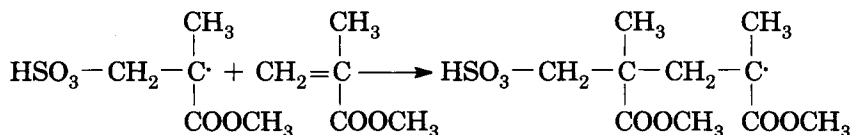


Fig. 5. Conversion Time Curves. ● in absence of $\text{Ca}_3(\text{PO}_4)_2$. (○) >> presence >> X >>>>> half-layer modification (●) >>>>> mono->>>>>. -----0°C; - - - - -45°C;50°C.

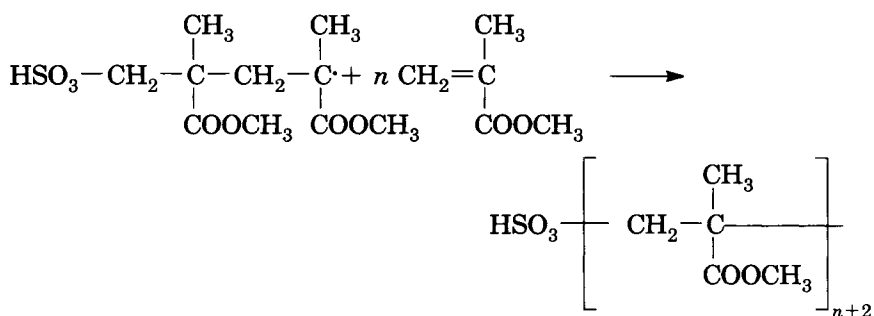
By disproportionation:



Propagation



and so on



In the case of absence of calcium phosphate, the initial rate was found to be 0.16×10^{-5} mol/L-s at 40°C; it increased to 0.6×10^{-5} mol/L-s in the presence of the same amount of modified $\text{Ca}_3(\text{PO}_4)_2$. After half- and monolayer modification, the rate increased to 1.39×10^{-5} and 1.67×10^{-5} mol/L-s, respectively. Increasing the temperature to 45 and 50°C increased the initial rate to higher values, as shown in Table V.

TABLE V

Ca ₃ (PO ₄) ₂	Temperature (°C)			Activation energy (J/mol)
	40	45	50	
—	0.16	0.20	0.20	54.34 × 10 ³
1 g unmodified	0.58	0.69	0.86	38.20 × 10 ³
1 g half-layer modification	1.39	1.51	1.85	25.78 × 10 ³
1 g monolayer modification	1.67	1.85	2.08	19.10 × 10 ³

^aInitial rate × 10⁵/mol/L=s.

The apparent activation energy E_a was calculated between three temperatures (40, 45, and 50°C) by plotting log initial rate versus $1/T$, the slope of the straight line determined, and E_a calculated:

$$E_a = \text{slope} \times 4.57$$

The apparent activation energy for the polymerization process in absence of substance was found to be 54.34×10^3 and 38.20×10^3 J/mol using 1 g unmodified calcium phosphate. Using 1 g of half-layer calcium phosphate resulted in decreasing the apparent activation energy to 25.78×10^3 J/mol; using 1 g of monolayer calcium phosphate resulted in a further decrease of the apparent activation energy to 19.1×10^3 J/mol.

The effect of modified calcium phosphate on the viscosity-average molecular weights of the polymers obtained was studied, and the data are given in Table VI. From Table VI it is found that the viscosity-average molecular weight was found to be 4.28×10^5 g/mol in the absence of calcium phosphate substance; it increased to 6.6×10^5 g/mol when 1.0 g unmodified calcium phosphate was used in the reaction mixture. The viscosity-average molecular weight of poly(methyl methacrylate) prepared under the same conditions but in the presence of half-layer modified calcium phosphate was found to increase to 7.32×10^5 g/mol and to 8.34×10^5 g/mol when monolayer calcium phosphate was modified with stearic acid.

TABLE VI
Effect of Modified Calcium Phosphate on the Viscosity-Average Molecular Weight M_v
of the Polymers Obtained After 3 h

Ca ₃ (PO ₄) ₂ (g)	Conversion (%)	[η] (dl/g)	$M_v \times 10^{-5}$ (g/mol)
0.0	25.1	1.41	4.28
1.0 unmodified	80.3	1.96	6.60
1.0 half-layer modification	90.8	2.12	7.32
1.0 monolayer modification	95.0	2.34	8.34

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