

Aqueous Polymerization of Methyl Methacrylate and Characterization of the Obtained Polymers in the Presence of *N,N*-Dioxalyl *p*-Amino Benzoyl *N,N*-Dioxalyl Urea and Its Fe(II) and Fe(III) Complexes

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SYNOPSIS

The emulsifier-free emulsion polymerization of methyl methacrylate (MMA) was studied using sodium bisulfite as initiator in the absence and presence of a new organic chelating agent, *N,N*-dioxalyl *p*-amino benzoyl *N,N*-dioxalyl urea, and its iron (II) and (III) complexes. The organic ligand with free carboxyl groups has a retarding effect on the polymerization reaction while its iron complexes have a catalytic effect. The mechanisms of the catalytic effect of iron complexes or the inhibition mechanism of the organic ligand are discussed. The effect of pH values on the polymerization processes was also investigated. The apparent energy of activation was found to be 4.99×10^4 J/mol, 6.38×10^4 J/mol, 4.46×10^4 J/mol, and 3.72×10^4 J/mol in the absence and in the presence of 0.5 g of ligand and 0.1 g of its Fe (II) and (III) complexes, respectively. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

It was previously reported that the aqueous polymerization of methylmethacrylate 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.² The different metal oxides also have a catalytic effect varying from ineffective³ to moderate⁴ to high.^{5,6} The aqueous polymerization of MAA was also carried out in the absence and in the presence of various inorganic-organic substances and complexes.⁷⁻¹² 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. Fractionation depending on the separation mechanism may be

classified into three categories, based on phase separation (Baker-Williams method¹³), adsorption (Mark-Satio method¹⁴) and molecular sieving (gel permeation chromatography, GPC¹⁵).

Thin-layer chromatography (TLC) can be applied to the fractionation of homopolymers according to their molecular weights.¹⁶⁻¹⁹ Separation by molecular weight can be attained predominantly through the phase separation phenomena that occur on a chromatoplate.^{18,19} A number of investigations have been carried out on the separation of homopolymers according to their molecular weights using the TLC technique, which has proved to be a very rapid and good technique for determination of the molecular weight distribution (MWD) of the polymers obtained.^{8,19-22}

In this work we studied the emulsifier-free emulsion polymerization of methylmethacrylate (MMA) in the presence of the organic ligand (*N,N*-dioxalyl *p*-amino benzoyl *N,N*-dioxalyl urea) and its iron (II) and (III) complexes. The effect of pH on the viscosity-average molecular weights obtained and molecular weight distributions by means of TLC, was also determined.

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EXPERIMENTAL

Materials

Methylmethacrylate monomer, a product of Merck-Schuchardt, was of 99% purity, stabilized with 100 ppm hydroquinone. It was washed with a small amount of (10%) sodium hydroxide and distilled water. The MMA was separated with a separating funnel, dried over anhydrous sodium sulfate, and finally distilled using a fractionating column of about 15 theoretical plates. The fraction boiling at 100–100.5°C was collected and used.

All chemicals and reagents used were pure research grades. The silica gel type (G 60), which contains gypsum (13.3%), was used as the stationary phase in TLC experiments.

Preparation of *N,N*-dioxalyl *p*-amino Benzoyl *N,N*-dioxalyl Urea and Its Fe(II) and (III) Complexes

The new organic chelating agent was prepared by condensation of *p*-amino benzoic acid (0.1 mol) and urea (0.1 mol) in a xylene medium, using a Dean and Stark apparatus. The theoretical amount of water was removed to produce *p*-amino benzoyl urea. Further condensation in the same medium of the product with oxalic acid (0.4 mol) for 7 h resulted in production of the *N,N*-dioxalyl *p*-amino benzoyl dioxalyl urea, which has a melting point of 246°C after crystallization from distilled water. The yield percentage was found to be 80.3%. The UV spectrum of the ligand showed an absorption band at $\lambda_{\max} = 282$ nm, which could be attributed to the $\pi-\pi^*$ transition (E_2 band) in the benzene ring. Another absorption band appearing at 212 nm may be due to the $\pi-\pi^*$ transition of C=O [cf. Fig. 1(a)]. The infrared spectrum shows the characteristic band of stretching vibrations of carbonyl group at 1680 cm^{-1} . A series of bands appears in the region 2880 to 2480 cm^{-1} and are attributed to the hydrogen bonded OH stretching vibrations in carboxylic acids. A sharp band appears at 3300 cm^{-1} , which could be attributed to the —NH stretching vibration. The medium band appearing at 3450 cm^{-1} could be attributed to the hydrogen bonded OH stretching vibration or NH stretching vibration, while the band appearing at 3560 cm^{-1} could be attributed to the free OH stretching vibration. The band appearing at 740 cm^{-1} could be attributed to the CH out-of-plane deformation in the benzene ring, and the band appearing at 780 cm^{-1} could be attributed to 1,4-disubstitution in the benzene ring [cf. Fig. 1(b)].

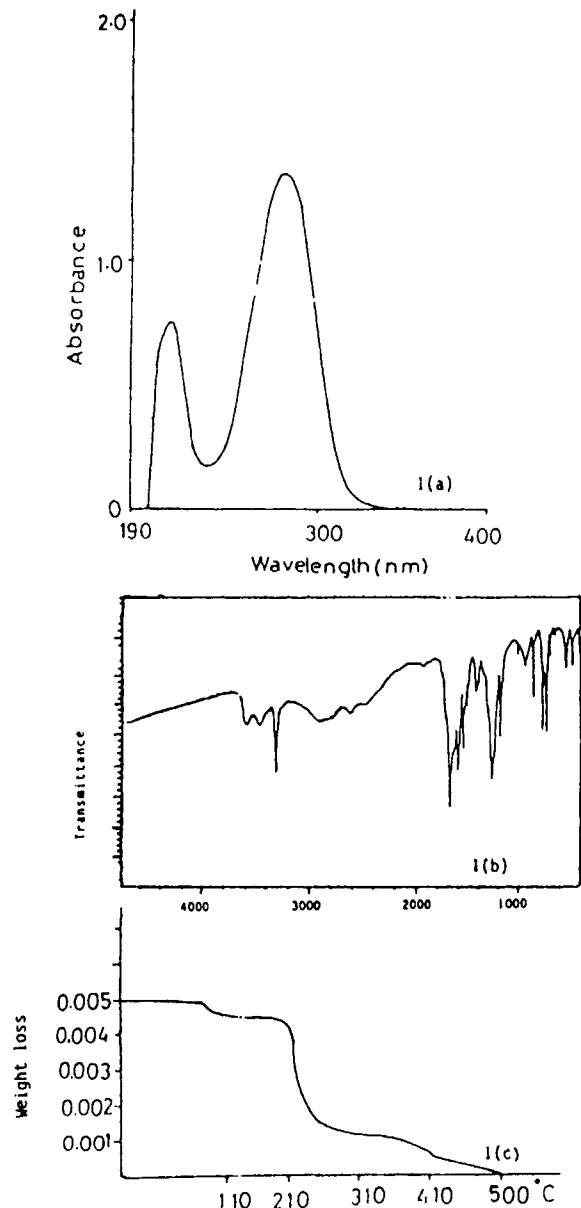


Figure 1 UV, IR spectra and thermogravimetric analysis of the organic ligand. (1a) UV spectrum, (1b) IR spectrum, (c) thermogravimetric analysis.

Thermogravimetric analysis (TGA) of the ligand, represented in Figure 1(c), was performed using a thermal analyzer (Shimadzu DT-30). The weight loss was measured from ambient up to 500°C. The weight loss for the ligand was calculated over the temperature range at which water molecules were expelled. The number of water molecules of crystallization are 4 per 1 mol of the investigated ligand, as indicated by the percentage weight loss from the TGA curve. Some other analytical data for the prepared ligand are given in Table I. Fe(II) and (III) com-

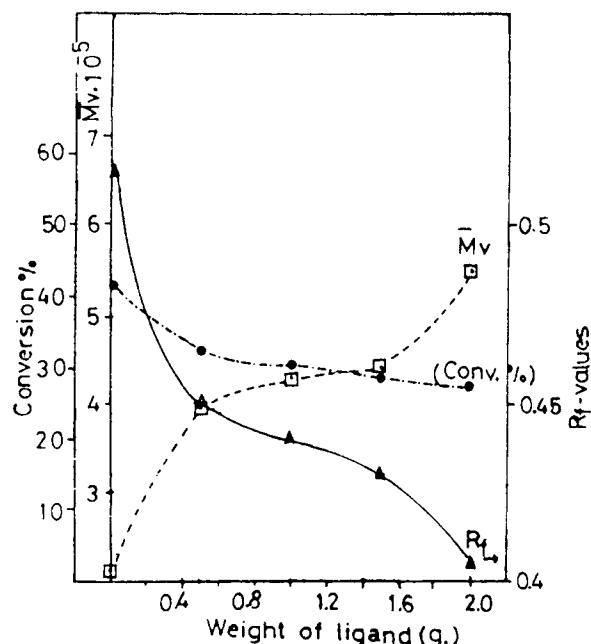


Figure 2 Conversion % M_v and R_f values vs. weight of ligand (for polymers obtained after 3 h at 40°C using initiator concentration 0.1 mol/L).

plexes of the tetra-functional organic ligand are prepared by dropwise addition of Fe(II) sulfate (water solution) or Fe(III) chloride (ethanolic solution) (0.02 mol/50 mL) to 50 mL water solution (0.01 mol) in the case of Fe(II), or 50 mL ethanolic solution, in the case of Fe(III), of the organic ligand. The mixture was refluxed for 3 h under nitrogen atmosphere and the products were filtered, washed with water and absolute ethanol, then dried to constant weight. Iron content was determined using an atomic absorption spectrophotometer SP 191. The chemical formulas of the organic ligand, its iron complexes, and other analytical data, are tabulated in Table I.

Emulsifier-Free Emulsion Polymerization

To a well-stoppered conical flask of 500-mL capacity, were put the amount of initiator in 200 mL distilled water followed by the organic ligand or iron complexes (when studying their effects). Finally the amount of monomer (MMA) (2.6 g) was added to the reaction mixture under nitrogen atmosphere. The order of addition of substances was kept constant in all the experiments performed. The conical flasks were then put in an automatically controlled thermostat at the required temperature. The flasks were shaken (15 shakings/10 s, every 15 min) for

definite periods of time. The reaction was stopped at will by the addition of a few drops of sodium hydroxide (5%) and cooling in an ice bath. The polymer, or mixture of polymer and organic ligand or its iron complexes, was then filtered using a Buchner funnel, washed thoroughly with distilled water and methanol, and finally dried in an electric oven at 105°C to constant weight.

Purification of the Polymer

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

Determination of Intrinsic Viscosity and Average Molecular Weights

The intrinsic viscosity $[\eta]$ for each polymer sample was determined by the usual method of extrapolation. The viscosity-average molecular weights \overline{M}_v for the respective polymers were calculated from the following equation:

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

The viscosity measurements were carried out in thiophene-free benzene at 25°C.²³

Thin-Layer Chromatographic Analysis

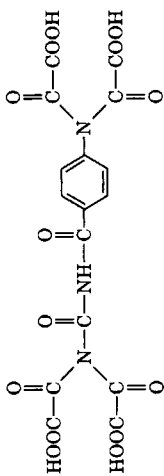
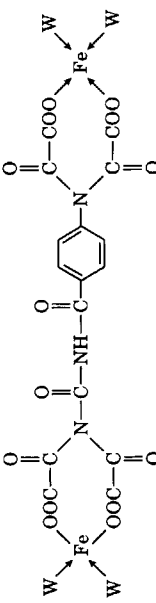
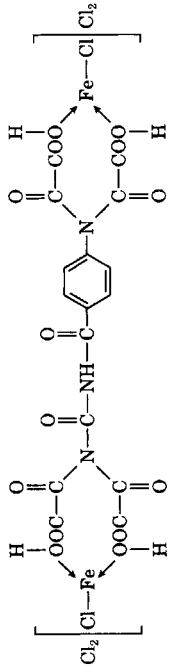
We have applied the TLC technique for characterization of poly(methylmethacrylate) (PMMA) samples obtained by emulsifier-free emulsion polymerization in the absence and in the presence of different amounts of iron complexes. TLC experiments were performed under the same conditions as described in a previous article.¹²

RESULTS AND DISCUSSION

Effect of Organic Ligand

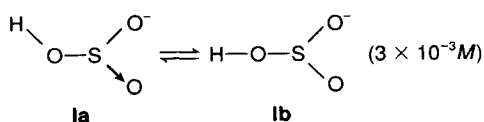
The organic ligand is partially soluble in water at 40°C. The polymerization of MMA (2.63 g) in water (200 mL) was performed using NaHSO₃ (0.1 mol/L) under nitrogen atmosphere at 40°C, in the absence (homogeneous polymerization system) or in

Table I Some Analytical Data of the Ligand and Its Iron Complexes

| Chemical and Molecular Formula of the Substance Used | Elemental Analysis (Calc./Found) | | | | Iron Content (wt.%) (Req./Found) | Molecular Weight (Req./Found) | Acid Value (Req./Found) | pK ₁ -pK ₄ Values |
|--|----------------------------------|--------------|--------------|----------------|----------------------------------|-------------------------------|-------------------------|---|
| | C | H | N | Fe | | | | |
|  $C_{16}H_{13}N_3O_4 \cdot 4H_2O$ | 35.62 34.90 | 3.15 2.85 | 7.80 7.30 | — — | — — | 467.00 446.00 | 479.60 499.00 | 3.2, 4.05 5.51, 8.70 |
|  $Fe_2(C_{16}H_{13}N_3O_{18})$ | 29.69 27.83 | 2.01 1.59 | 6.49 5.83 | — — | 17.27 16.82 | 646.70 610.00 | — — | — — |
|  $Fe_2(C_{16}H_{13}N_3Cl_6O_{14})$ | 24.25 22.56 | 1.14 1.02 | 5.30 4.97 | 26.91 26.32 | 14.11 13.68 | 745.70 780.00 | — — | — — |

the presence of different amounts of ligand (heterogeneous system). The pH of the reaction medium in all polymerization reactions was approximately 3. The conversion percentage of the monomer to polymer in absence of organic ligand was found to be 41.5% after 3 h. The conversion percentage after 3 h was also determined for systems containing different amounts of organic ligand. The data are graphically represented in Figure 3: the decrease in the conversion percentage is due to the presence of the organic ligand with four carboxylic groups in its structure. This means that the organic ligand has an inhibiting effect on the emulsifier-free emulsion polymerization of MMA. The ionization of the ligand in aqueous medium leads to the formation of hydrogen ions in solution, which consequently affects the ionization of NaHSO_3 , that is, less radical formation occurs.

In the absence of ligand at low concentrations of sodium bisulfite



At higher concentrations (more than $10^{-2}M$)

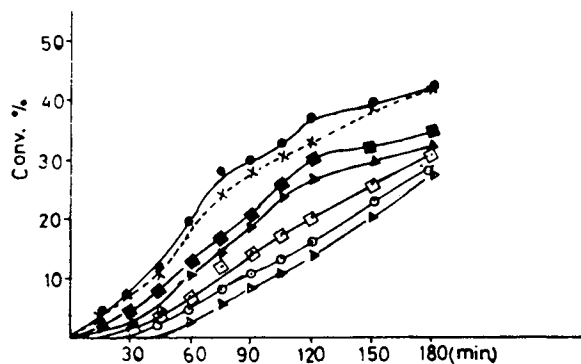
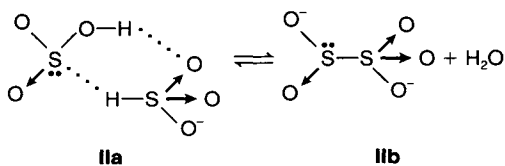
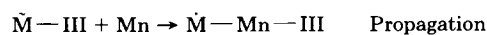
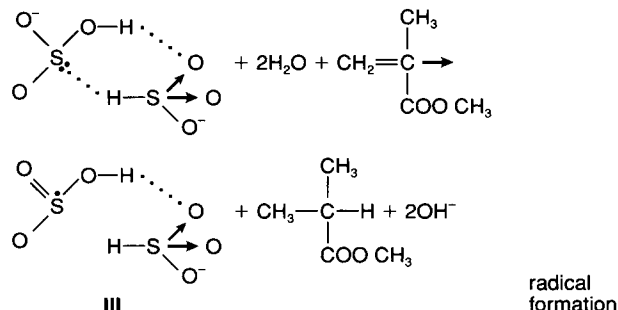
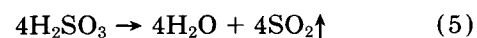
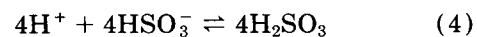
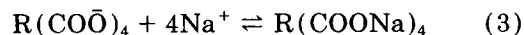
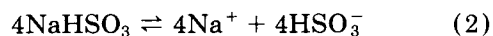


Figure 3 Conversion time curve in the absence and presence of different ligand quantity. (—X—X) without at 40°C ; (—▲—▲) in presence of 0.5 g ligand at 40°C ; (—□—□) in presence of 1 g ligand at 40°C ; (—○—○) in presence of 1.5 g ligand at 40°C ; (—△—△) in presence of 2 g ligand at 40°C ; (—■—■) in presence of 0.5 g ligand at 45°C ; (—●—●) in presence 0.5 g ligand at 50°C .

The above equilibrium is shifted to the left in the aqueous polymerization reaction; therefore, the following scheme can be suggested to explain the mechanism of radical formation.



In the presence of organic ligand:



where $\text{R} = \text{C}_{12}\text{H}_5\text{N}_3\text{O}_6$.

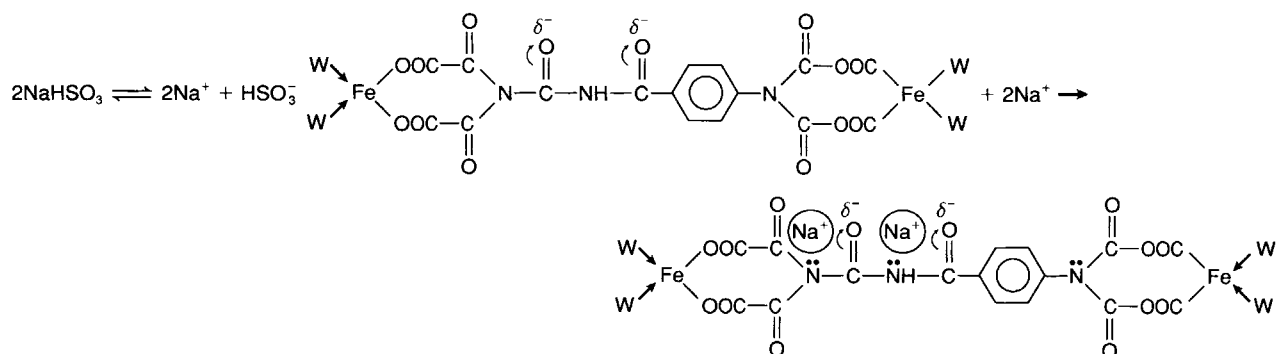
The first ionization step of the initiator could be effected by the above ionization reactions of the organic ligand in aqueous medium. The viscosity-average molecular weight of the polymers obtained in the presence of different amounts of organic ligand was found to increase with the increase of ligand quantity, while the R_p values were found to decrease. This is due to fewer radicals being formed during the polymerization reaction in presence of organic ligand. The polymer produced is in a powder form mixed with the organic ligand. The mixed powder was filtered and dried in an oven at 105°C , then dissolved in benzene to separate polymer from ligand, which is not soluble in benzene. The conversion percentage of monomer to polymer was calculated with time in the presence of different amounts of organic ligand. The data are graphically represented in Figure 3. From the kinetic curves (conversion % vs. time), it is clear that organic ligand

has an inhibiting effect on the polymerization reaction and that the induction period of the reaction increases with the increase of organic ligand quantity. The initial rate of polymerization was determined by taking the slope of the conversion time curve up to 10% conversion to avoid complications due to the increasing solids content in the reaction medium. The rate = $P/V \times Mt$ mol/L s, where P is the weight of polymer formed in time (t) in seconds, (V) is the volume of the aqueous phase in liter, M is the molecular weight of monomer. From Figure 3, it was also found that the initial rate of polymerization in the presence of organic ligand increases with increasing reaction temperature.

Effect of Iron Complexes

The emulsifier-free emulsion polymerization of MMA (2.6 g) in water (200 mL) was performed under nitrogen atmosphere using NaHSO_3 (0.1 mol/

L) as initiator at 40°C in the absence and in the presence of different amounts of Fe(II) and Fe(III) complexes of *N,N*-dioxalyl *p*-amino benzoyl *N,N*-dioxalyl urea. The conversion percentage, viscosity-average molecular weights, and R_f values on TLC plates for the polymer samples obtained after 3 h, were determined. The data are graphically represented in Figure 4, from which it is clear that the conversion percentage increases from 41%, in the absence of iron complexes, to 66 and 79% in the presence of 0.1 g of Fe(II) and (III) complexes, respectively. This indicates that the Fe(II) and (III) complexes have a catalytic effect but with higher values in the case of Fe(III) complex, which is in good agreement with that found by Moustafa et al.²⁴ in the case of phthalocyanine complexes, and Sayyah et al.¹² in the case of nickel complexes of tetra-oxalyl *p*-phenylene diamine. The catalytic effect of Fe(II) complex can be explained on the basis of the following equation:



The attraction of sodium ions to the partially negatively charged oxygen atoms of $\text{C}=\text{O}$ groups leads to more ionization of NaHSO_3 in aqueous medium and consequently to more radical formation (i.e., catalytic effect of Fe(II) complex. In the case of the Fe(III) complex (partially soluble in water), the catalytic effect could be attributed to the presence of two labile chloride ions on each side of the complex (the structure in Table I), which are attracted more easily to the electropositive sodium ions of the initiator, leading to more ionization of the initiator and a greater catalytic effect than in the case of Fe(II) complex. Mössbauer effect measurements for the Fe(III) complex were performed before and after the polymerization reaction. The data obtained tell us that the iron state in the complex is unchanged. This means that sodium bisulfite has no effect on the iron state in the complex (cf. Fig. 5).

The viscosity-average molecular weight decreases with increasing iron complex quantity up to 1.0 g, then increases with higher iron complex quantities. The viscosity-average molecular weights are higher in the case of polymer samples prepared in the presence of Fe(II) complex. The R_f values of the obtained polymer samples, in the presence of different amounts of iron complexes, were found to be in good agreement with the viscosity data. The R_f values increase, in all cases, in the presence of iron complex up to 1.0 g, then decrease up to 2.0 g. The R_f values of the polymer samples obtained in the presence of the same amounts of iron complex were found to be higher in the case of Fe(III).

The thin-layer chromatograms for the polymer samples prepared in the absence and in the presence of different amounts of iron complexes [Fe(II) and Fe(III)] are represented in Figure 6(I) and (II).

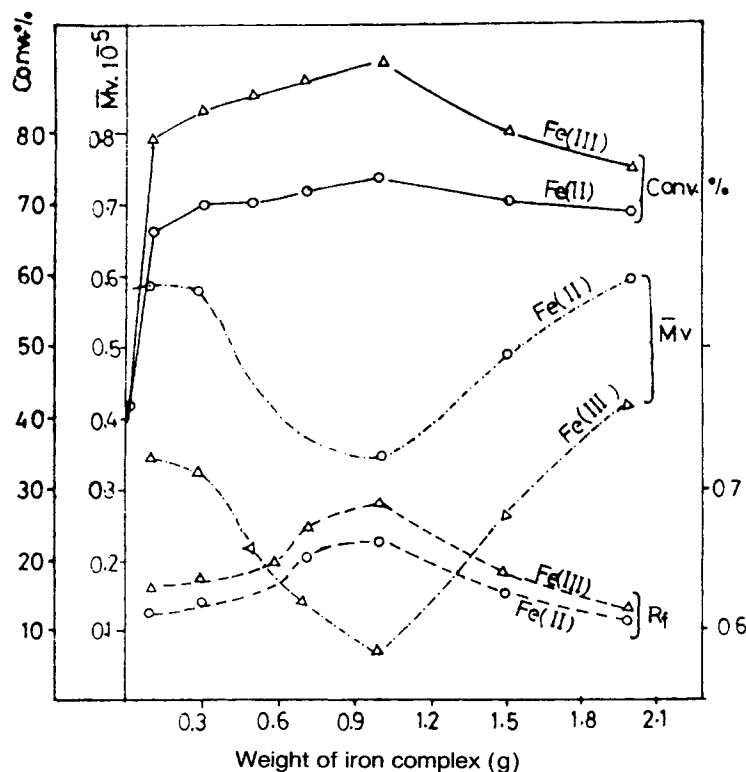


Figure 4 Conversion % \bar{M}_v and R_f values vs. weight of complex (for polymers obtained after 3 h at 40°C using initiator concentration 0.1 mol/L).

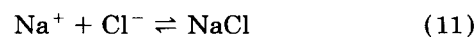
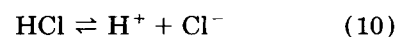
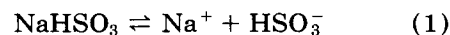
From the chromatograms it is clear that both the spot areas and R_f values for polymer samples prepared in the presence of 0.1 g iron complex are higher than those for polymer sample obtained in the absence of iron complex; this means a decreased viscosity-average molecular weight and increased polydispersity. The increase of the amount of iron complex in the reaction medium up to 1.0 g leads to an increase in the R_f values and the spot areas of the polymer samples obtained. Higher amounts of iron complex, up to 2.0 g, lead to a decrease in the R_f values and spot areas on the chromatoplates. Consequently, the polydispersity of the polymer samples obtained decreases with increasing iron complex amounts from 1.0 up to 2.0 g. The polydispersity of samples obtained in the presence of Fe(III) complex is higher than those obtained in the presence of Fe(II) complex using the same amount of the iron complex. The lowest polydispersity was found for polymer samples obtained in the presence of 0.1 g of iron complexes. (Sample b in both chromatograms).

Effect of pH Values

The emulsifier-free emulsion polymerization of MMA in water was carried out using different pH values, by addition of HCl or acetic acid and am-

monium hydroxide for pH adjustment, in the presence of NaHSO_3 (0.1 mol/L) as initiator at 40°C. The conversion percentage, viscosity-average molecular weight, and R_f values were calculated at different pH values varying from 1.25 to 7.00. The data are graphically represented in Figure 7. From Figure 7 it is clear that the highest conversion percentage was found at pH 3.0. The conversion percentage after 3 h was found to increase from pH 1.25 up to pH 3.0, then the conversion percentage decreased once more up to pH 7.0. The viscosity-average molecular weights of the polymers obtained after 3 h were measured, calculated, and are graphically represented in Figure 7 with variation of pH values of the reaction medium. The \bar{M}_v values were found to decrease from pH 1.25 up to pH 3.0, then increased from pH 3 to pH 4.25, then decreased once more from pH 4.25 up to pH 7.0. This behavior of conversion percentage and viscosity-average molecular weight can be explained as follows:

At pH 1.25 (addition of HCl solution to the reaction medium):



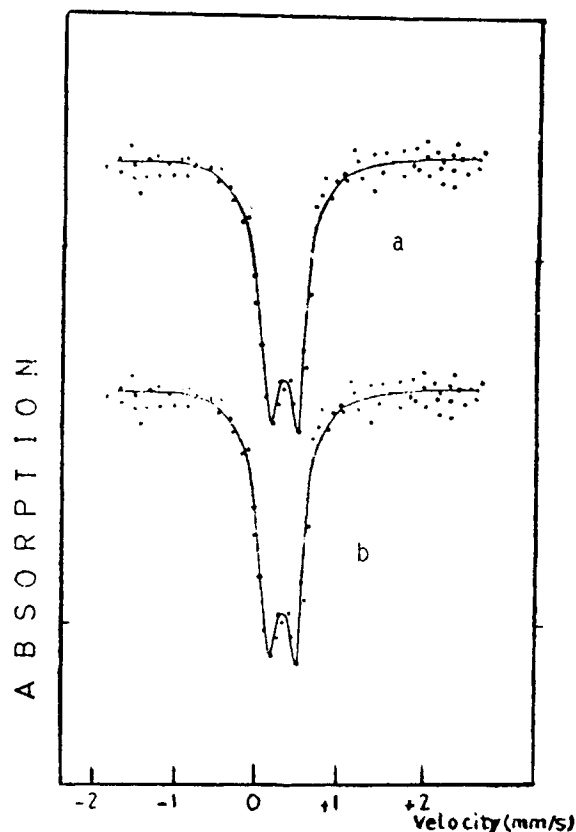
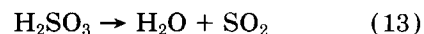


Figure 5 Mössbauer spectrum of ferric state complex: (a) before the polymerization reaction and (b) after the polymerization reaction.



The increase of hydrogen ion concentration in the reaction medium leads to the neutralization of bisulfite ions formed in Eq. (1), leading to a decrease in the bisulfite ions concentration [Eqs. (10)–(13)] and consequently to a decrease in the bisulfite radicals formed according to Eq. (2). The conversion percentage will be decreased and the viscosity-average molecular weight of the formed polymer will increase more than in the case of pH 4.25 (without any additives).

At pH 3.0 (weak acid medium), this value of pH seems to be suitable for ionization of sodium bisulfite. Therefore, more bisulfite radicals should be formed in the reaction medium, leading to an increase in the conversion percentage and a decrease in the viscosity-average molecular weight.

At pH 4.25 (without any additives in the reaction medium), the conversion percentage decreased once more. This is due to less formation of bisulfite ions, which means that the ionization of sodium bisulfite at this pH value is less than at pH 3.0.

At neutral pH, or slightly alkaline values, the OH^- concentration will be increased, and consequently the equilibrium in Eq. (2) will be shifted to the left, i.e., less radical formation and less conversion percentage.

Table II. Effect of Temperature on the Emulsifier-Free Emulsion Polymerization of MMA in the Absence and Presence of 0.5 g Organic Ligand and 0.1 g of Its Iron Complexes Using (0.1 mol/L) NaHSO_3

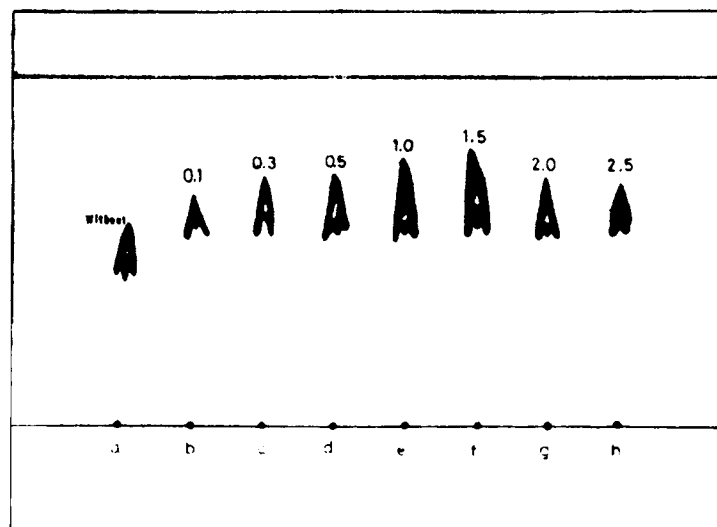
| Temperature (°C) | Initial Rate $\times 10^{-6}$ (mol/L s) | Activation Energy $\times 10^{-4}$ (J/mol) | $\bar{M}_v \times 10^{-5}$ | R_f Values |
|------------------|--|---|----------------------------|--------------|
| 40 ^a | 7.71 | | 2.120 | 0.515 |
| 45 ^a | 10.96 | 4.99 | 1.988 | 0.535 |
| 50 ^a | 14.40 | | 1.655 | 0.560 |
| 40 ^b | 5.88 | | 3.990 | 0.450 |
| 45 ^b | 8.12 | 6.38 | 3.532 | 0.455 |
| 50 ^b | 11.78 | | 2.950 | 0.465 |
| 40 ^c | 17.34 | 4.46 | 0.595 | 0.615 |
| 45 ^c | 24.54 | | 0.480 | 0.630 |
| 50 ^c | 31.95 | | 0.434 | 0.650 |
| 40 ^d | 25.58 | | 0.345 | 0.630 |
| 45 ^d | 31.98 | 3.72 | 0.287 | 0.645 |
| 50 ^d | 40.83 | | 0.197 | 0.676 |

^a In absence of catalyst.

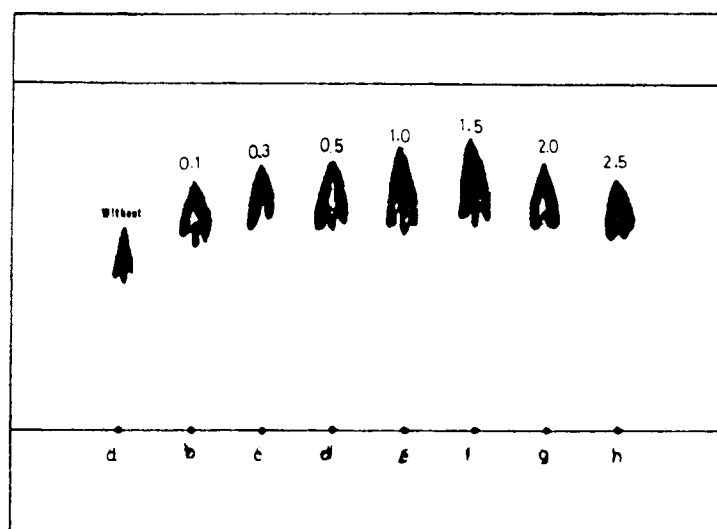
^b In presence of (0.5 g) organic ligand.

^c In presence of (0.1 g) Fe(II) complex.

^d In presence of (0.1 g) Fe(III) complex.



Fe(II) complex



Fe(III) complex

Figure 6 Thin-layer chromatogram for polymers obtained after 3 h in the absence and presence of Fe(II) and III complexes.

Effect of Temperature

The emulsion polymerization of MMA (2.6 g) in water (200 mL) using NaHSO_3 (0.1 mol/L) as initiator in nitrogen atmosphere, in the absence and presence of 0.5 g of ligand or its Fe(II) and Fe(III) complexes, for different periods of time with mild shaking (15 shakings/10 s every 15 min) was carried out at different temperatures (40, 45, and 50°C).

The data are graphically represented in Figure 8. The viscosity-average molecular weights and R_f values were measured for polymer samples obtained after 3 h, and the data are summarized in Table II. It was found that the initial rates (R_i) of the polymerization reactions increase with increasing reaction temperature (cf. Fig. 8). The initial rate of the polymerization reaction at the same temperature increases in the following order:

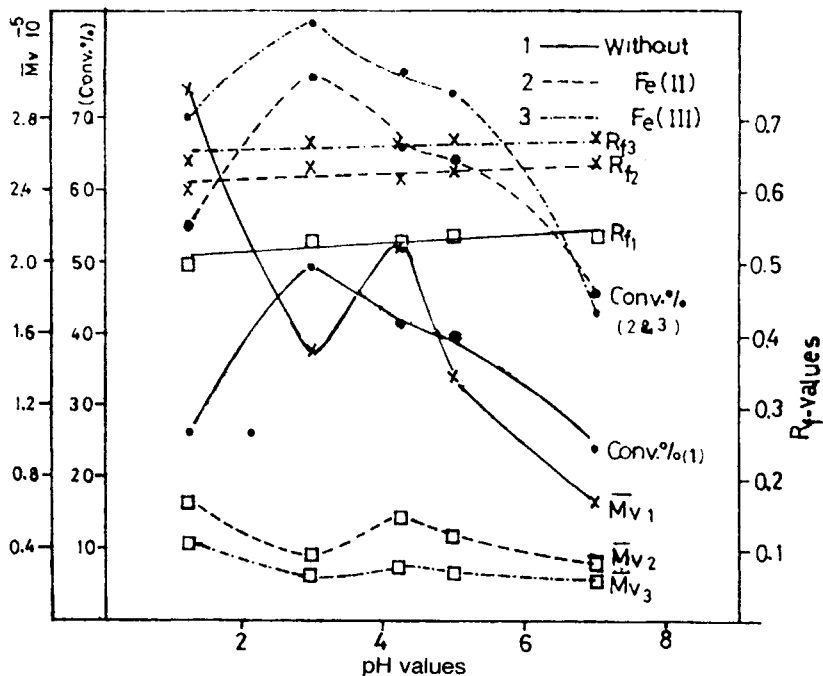


Figure 7 Effect of the pH values of the reaction medium on the conversion percent, \bar{M}_v , and R_f values of the polymers obtained at 40°C.

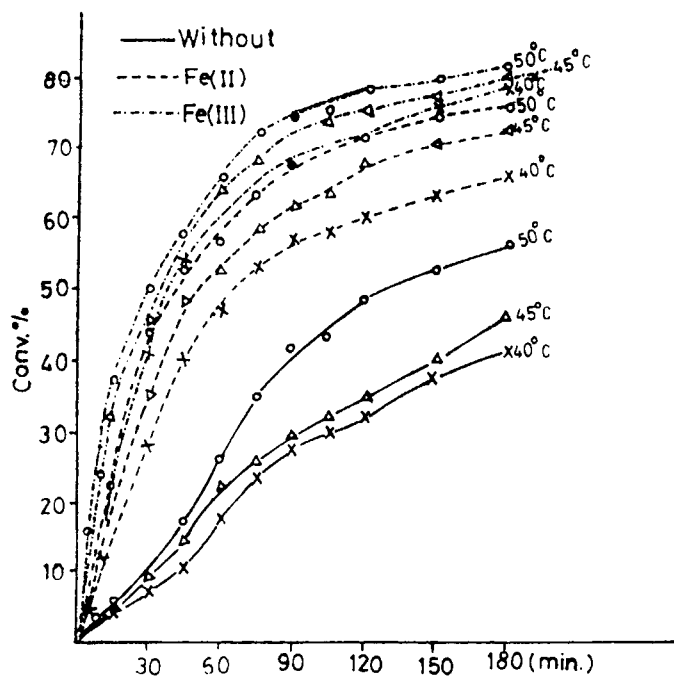


Figure 8 Conversion time curve in the absence and presence of 0.1 g of Fe(II) or (III) complex at different temperatures.

$$R_i(\text{MMA})_{\text{ligand}} < R_i(\text{MMA})_{\text{without additives}}$$

$$< R_i(\text{MMA})_{\text{Fe(II) complex}} < R_i(\text{MMA})_{\text{Fe(III) complex}}$$

In all cases the initial rate and conversion percentage increase while the \overline{M}_v values decrease with higher reaction temperature (cf. Table II). The R_f values increase with higher reaction temperature, which confirms the viscosity measurements.

The apparent activation energy (E_a) of different polymerization systems was calculated between three temperatures (40, 45, and 50°C). The data are also given in Table II. The E_a values decrease in the following order:

$$\text{Ligand} > \text{absence} > \text{Fe(II) complex}$$

$$> \text{Fe(III) complex}$$

CONCLUSION

The pH value of the reaction medium has an effect on the polymerization rate, \overline{M}_v values of the obtained polymer, and R_f values on the chromatoplate. This effect is noticed in the absence and presence of iron complexes but with higher values of the reaction rates in the presence of iron complexes. The iron complexes catalyzed the polymerization of MMA, while the ligand inhibited the polymerization processes. Higher catalytic effect is noted using Fe(III) complex as a catalyst.

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