

Some observations in the aqueous polymerizations of methyl methacrylate (MMA) initiated by the redox systems Fe^{2+} - $\text{S}_2\text{O}_8^{2-}$ and Fe^{2+} - H_2O_2

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It has been observed in the aqueous polymerizations of methyl methacrylate (MMA) initiated by the redox system, ferrous ammonium sulphate (FAS)-potassium persulphate (KPS), that at 10°C or below, the separating polymer phase is always a milky white precipitate remained suspended in the aqueous phase, while above 20°C, the polymer phase is a stable colloid and is yellow in colour (light or deep, depending on the concentration of the reactants, 10^{-5} to 10^{-3} mol/dm³). The colloid stability of the latex solutions increases with the rise in temperature in the range 20 to 50°C. Between 10 to 20°C, the separating polymer phase is partly colloidal and partly coarse precipitate. If the polymerization is initiated by the Fenton's reagent (Fe^{2+} - H_2O_2), under identical experimental conditions, the polymer phase is always a precipitate in the temperature range 4 to 50°C. At or below 10°C, the latex particles are milky white, but above 10°C the particles are yellowish. It is suggested that the complex ions $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ and $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2(\text{H}_2\text{O})_4\text{Fe}]^{4+}$, produced in the systems during the reactions (depending on temperature and pH of the solution), are strongly adsorbed by the polymer molecules (PMMA)/latex particles, having sulphate ($-\text{O}-\text{SO}_3^-$) end groups (polymer from the KPS-MMA-FAS system), through the electrostatic interactions, and act as peptisers to the lyophobic polymer colloids. In the Fe^{2+} -MMA- H_2O_2 system, the polymers having neutral OH end groups, do not adsorb strongly the positively charged ferric ion complexes. The purified polymers (PMMA) are found to contain iron.

It has been reported¹⁻³ that Fe^{2+} - $\text{S}_2\text{O}_8^{2-}$ and Fe^{2+} - H_2O_2 systems are very efficient redox initiators of vinyl polymerizations in aqueous solutions. Kinetics of the polymerization reactions have been analysed through the conventional steady state hypothesis¹⁻⁸, in spite of the fact that the initiation reaction³, viz., $\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{3+} + \text{SO}_4^- + \text{SO}_4^{2-}$, has very short half life (about 12.5 s at 25°C, when $[\text{Fe}^{2+}] = [\text{S}_2\text{O}_8^{2-}] = 10^{-3}$ mol dm⁻³). Under identical conditions, the half life of the reaction¹⁻³, $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}$, is also very short, about 14.39 s. Hence the assumptions of steady states in these systems are not valid, except at zero conversions during polymerizations.

It was first observed in this laboratory⁹ that in aqueous polymerizations of methyl methacrylate (MMA) initiated by the redox system, Fe^{2+} - $\text{S}_2\text{O}_8^{2-}$, in the temperature range 5 to 50°C in the absence of detergents, the separating polymer phase was a coarse milky white precipitate at or below 10°C. From 10 to 20°C, the polymer was partly colloidal and partly precipitate. Above

20°C, the polymer phase was a very stable yellow colloid.

In the present investigation, the above reactions have been studied in detail. A brief investigation of the Fe^{2+} -MMA- H_2O_2 system has also been made in order to understand the results of the Fe^{2+} -MMA- $\text{S}_2\text{O}_8^{2-}$ system. Some results of the aqueous polymerizations of MMA initiated by these two redox systems, are reported here.

Materials and Methods

The reagents, viz. ferrous ammonium sulphate (FAS), potassium persulphate (KPS), hydrogen peroxide, potassium sulphate, methyl methacrylate (MMA), sulphuric acid, and sodium hydroxide etc. were of BDH, E. Merck (Germany), E. Merck (India), AR/GR grade. They were purified further by the standard methods¹⁰ wherever possible. Hydrogen peroxide containing phosphoric acid as a stabiliser, was used as such. The monomer was purified and fractionated in vacuum by the method of Fitch *et al.*⁸ The fraction of MMA used for polymerization had a refractive index

1.4147 at 25°C, and was found to be 99.99 per cent pure by gas chromatographic analysis. Polymerizations were carried out in a round bottom corning flask (1 litre) fitted with nitrogen passing and sampling system during the reaction, and Hg-seal stirrer¹⁰. If the polymer was a precipitate during the reaction, the polymerizations were then carried out in 250 ml pyrex conical flasks in nitrogen atmosphere¹¹. Per cent conversion of monomer to polymer as a function of time was determined gravimetrically^{11,12}. Molecular weights of polymers were estimated viscometrically¹⁰⁻¹². pH of the solutions was measured with a Systronics' differential pH-meter. The colloid stability (CS) of the latex solutions was measured by the methods of Palit and Guha¹³, and Ottewill¹⁴, and the CS values were expressed as minimum quantity of MgSO₄ (in mmol/dm³) required to coagulate a given sample of polymer colloid.

Freshly prepared polymer (PMMA) was washed thoroughly first with HCl (N), followed by hot NaF (1.0 per cent, w/w) solutions, and finally with hot distilled water, till the filtrate became free from iron (+2 and +3 state) and fluorides. The apparently white wet polymer was then dried to a constant weight in a vacuum oven at 40°C. About 1.0 g of the polymer was completely burnt in a silica crucible. The nitric acid extract of the polymer ash was analysed using a spectrophotometer (Shimadzu UV-vis-2100) by the thiocyanate method of Vogel¹⁵ at $\lambda = 480$ nm. The dried polymer was found to be pale yellow in colour.

The intrinsic viscosity (η) of the polymer was estimated in a modified Ubbelohde viscometer¹⁰ at $(30 \pm 0.01)^\circ\text{C}$ in benzene solvent, and the molecular weights of polymers ($\bar{M}_v$) were calculated using the equation¹⁶,

$$(\eta) \text{ in ml/g} = 4.30 \times 10^{-5} \times (\bar{M}_v)^{0.787}$$

Results and Discussion

Some typical results of the polymerization reactions are shown in Fig. 1 and Table 1. In the

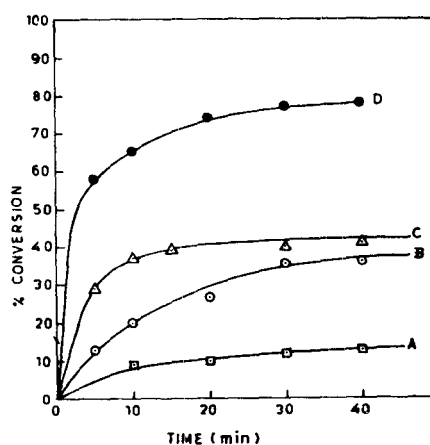


Fig. 1—Per cent conversion of MMA as a function of time (t). [MMA] = 0.0936 mol dm⁻³, [KPS] = [FAS] = 10⁻³ mol dm⁻³; curve D at 10°C while C at 40°C. [MMA] = 0.0936 mol dm⁻³, [H₂O₂] = [FAS] = 10⁻³ mol dm⁻³; curve B at 10°C while A at 40°C.

Table 1—Per cent conversion, colloidal stability (CS), pH change (i.e. ΔpH), conductivity change (Δk) of the reaction mixture during polymerization reactions and ($\bar{M}_v$) of the polymers

System A: [KPS] = [FAS] = 10⁻³ mol dm⁻³ and [MMA] = 9.36 × 10⁻² mol dm⁻³;

System B: [H₂O₂] = [FAS] = 10⁻³ mol dm⁻³ and [MMA] = 9.36 × 10⁻² mol dm⁻³

Temp. °C	NaF (added) in mol/ dm ³)	Nature of Latex	$\Delta\text{pH} =$ (pH) _{30 min} - (pH) _{initial}	$\Delta k \times 10^3$ (mho · cm ⁻¹)	CS (mmol/dm ³)	Per cent conversion (in 0.5 h)	($\bar{M}_v$) × 10 ⁻⁴
System A							
40	—	Yellow colloid	(~) 0.20	0.20	10.55	40.58	1.10
40	5 × 10 ⁻³	Colourless colloid	not measurable	0.35	5.66	31.20	0.79
30	—	Yellow colloid	(-) 0.10	0.10	5.40	62.70	2.01
10	—	White precipitate	not measurable	0.00	—	77.15	3.33
System B							
40	—	Yellow precipitate	0.00†	0.00	—	12.55	4.09
30	—	Yellow precipitate	0.00†	0.00	—	12.55	4.28
10	—	White precipitate	0.00†	0.00	—	40.54	4.69

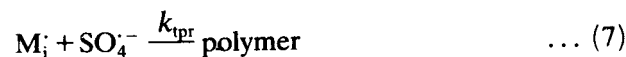
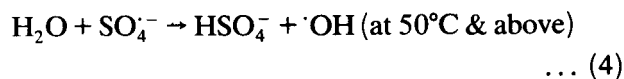
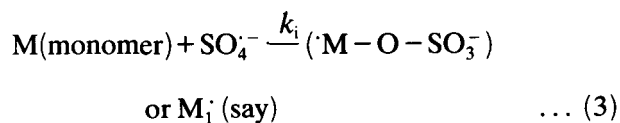
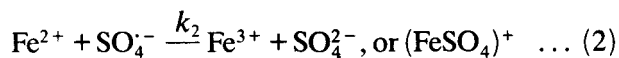
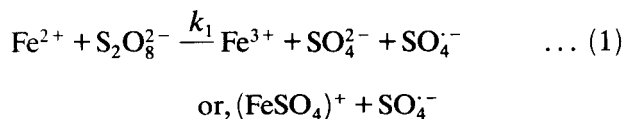
†H₂O₂ contains phosphoric acid as stabiliser.

KPS-FAS system, it was found that at 10°C the polymer was a white precipitate, while at 40°C it was a yellow colloidal solution. The rate of polymerization at 10°C was much higher than that at 40°C (Fig. 1). If the polymerization was carried out in the presence of NaF (in excess), the latex solution became colourless, but its colloidal stability (CS) was found to decrease. No measurable pH change was detected but the conductance of the latex solution increased. The time average rate of polymerization (defined as yield of polymer in 30 min/30 min) decreased in the presence of NaF (Table 1), and ($\bar{M}_v$) of the polymer also decreased.

In the absence of NaF, pH of the latex solution was found to decrease, whereas the conductance increased. The rates of polymerizations were found to decrease with the rise of temperature, but the (CS) increased (Table 1). At 10°C, there were no measurable changes of pH and of conductance of the latex solution during polymerization (Table 1).

In the Fenton's reagent system, the separating polymer phase was always a precipitate, and the polymer could be made white by washing with dilute solutions of HCl acid followed by NaF solution and hot distilled water. There was no measurable pH change during the reaction (Table 1).

The reaction mechanism in Scheme 1 is found to explain satisfactorily the observations stated above in the aqueous polymerization of MMA in the KPS-MMA-FAS system.



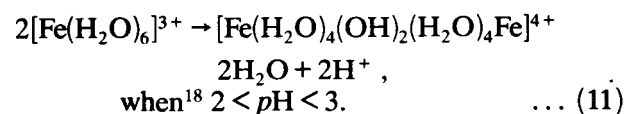
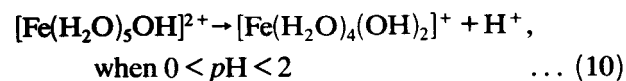
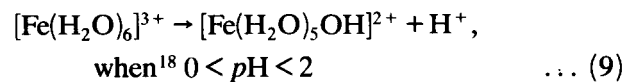
Scheme 1

OH free radical produced in (4) will take part in polymerizations and reactions (3) and (4) would account for sulphate and hydroxyl end groups in polymers^{2,4}. Besides, hydrolysis of sulphate groups in polymers would also account for OH end groups in polymers².

Since the reactions (1) and (2) are very fast in aqueous solutions¹⁻³ most of the $\text{S}_2\text{O}_8^{2-}$ ions would disappear via these reactions², and so the reactions of the monomer (MMA) and of water soluble oligomeric/polymeric free radicals, $(\text{M}_j)_{\text{w}}$, with the $\text{S}_2\text{O}_8^{2-}$ ions^{12,17} would not be important under the experimental conditions, particularly at lower temperatures (below 20°C). It is known that the chain transfer to monomer in aqueous polymerization of MMA is not important^{1,2,8}.

It has been observed that when ferric nitrate (solid) was added to HNO_3 solution (2N) at 25°C or 10°C, the mixture remained colourless, indicating that the species, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, is colourless^{18,19}. If however, FAS solid is added to KPS solution below 10°C, very faint yellow colour develops, possibly due to the formation of the complex ion¹⁸⁻²⁰, $(\text{FeSO}_4)^+$. Again when solid ferric nitrate is added to ice cold distilled water, the solution appears to be colourless. This shows that hydrated ferric ion, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ would be formed in aqueous solution in the temperature range 0 to 10°C. This ion is known to form at 25°C in aqueous solutions¹⁸⁻¹⁹ of pH ≤ 0.

At higher temperatures (20°C and above) and higher pH (0 to 4.0) various types of aqueous hydroxy ferric ions are known to be formed¹⁸⁻²⁰, viz.:



The formation of these ferric complexes is signalled by the changes in pH and conductances of the solutions (Table 1) and also by the colour changes of the solution. At or below 10°C, the reaction medium remains colourless, and there is

no change in pH during the reactions, indicating that the reactions (9) to (11) are not important.

At lower temperatures (10°C or less), rates of polymerizations and molecular weights of polymers were higher (Table 1). This means that most of the $\text{SO}_4^{\cdot -}$ radicals would disappear mainly via reactions (3), and to a small extent via reaction (2). The stationary concentrations of the primary radicals would be less, and hence reactions (7) and (8) would not be important at lower temperatures. Assuming that the chain transfer to monomer in the aqueous polymerization of MMA would not be important^{1,2}, polymerization rate equation (12) in the steady state (R_p) has been deduced:

$$R_p = k_p \left\{ \frac{(k_i)}{2k_{tp}} \right\}^{0.5} \beta^{-1} [M]_w^{1.5} \left[\frac{k_1[\text{Fe}^{2+}]_w [\text{S}_2\text{O}_8^{2-}]_w}{k_2[\text{Fe}^{2+}]_w + k_i[M]_w} \right]^{0.5} \times (V_w V_p)^{0.5} \quad \dots (12)$$

where, β (distribution coefficient of monomer) = $[M]_w/[M]_p$; V_w = volume fraction of the aqueous phase, V_p = volume fraction of the polymer phase, and $V_w + V_p = 1.0$, k_{tp} = termination rate constant in the latex phase, $[M]_w$ = monomer concentration in the aqueous (w) phase, and $[M]_p$ = monomer

concentration in the latex polymer (p) phase. Since polymerizations occur at high speeds (Fig. 1) at 10°C, it seems that under this condition,

$$\{k_i[M]_w\} > \{k_2[\text{Fe}^{2+}]_w\}$$

and Eq. (12) then predicts that

$$R_p \propto [M]_w^{1.0} [\text{Fe}^{2+}]_w^{0.5} [\text{S}_2\text{O}_8^{2-}]_w^{0.5} \quad \dots (13)$$

whereas at high temperatures, or at high concentrations of Fe^{2+} ions at any temperature, the rates of polymerizations decreased, and so it appears that under this condition,

$$\{k_2[\text{Fe}^{2+}]_w\} > \{k_i[M]_w\},$$

where,

$$R_p \propto [M]_w^{1.5} [\text{Fe}^{2+}]_w^0 [\text{S}_2\text{O}_8^{2-}]_w^{0.5} \quad \dots (14)$$

in the absence of any other complications.

At 10°C, the measured reaction orders of the reactants (Fig. 2) are shown in Eq (15). Time average rate (v_p') may be written as

$$V_p' (\text{experimental}) \propto [M]_w^{1.17} [\text{S}_2\text{O}_8^{2-}]_w^{0.47} [\text{Fe}^{2+}]_w^{0.51} \quad \dots (15)$$

while at 40°C (Fig. 3), the orders are shown in

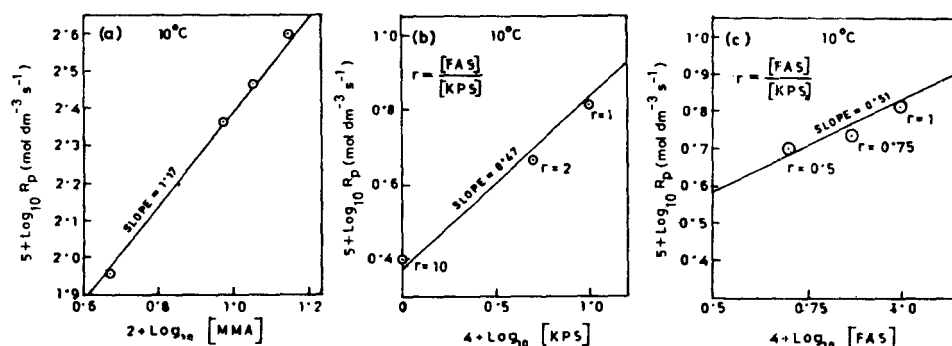


Fig. 2—Order plot of the reactants (at 10°C): (a) monomer order: $[\text{FAS}] = [\text{KPS}] = 10^{-3}$ mol/dm³; $[\text{MMA}] = 0.104$ mol dm⁻³; (b) KPS order: $[\text{MMA}] = 0.1404$ mol dm⁻³, $[\text{KPS}] = 10^{-3}$ mol/dm³; $[\text{FAS}]$ varies (5×10^{-4} to 1×10^{-3} mol/dm³).

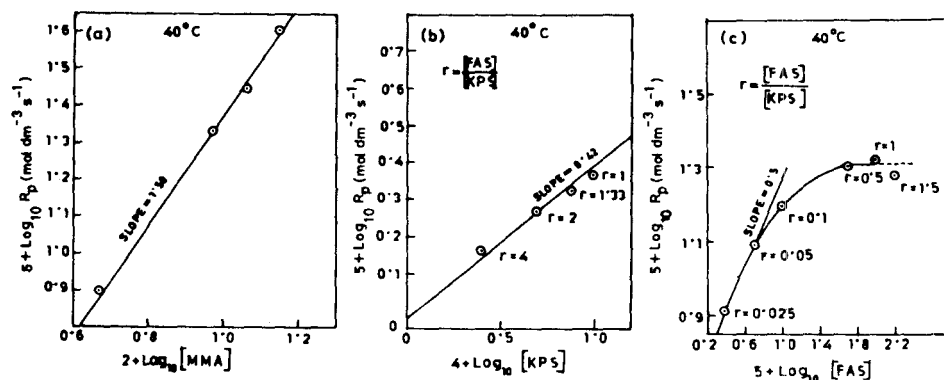


Fig. 3—Order plot of the reactants at 40°C. (a) Monomer order: $[\text{FAS}] = [\text{KPS}] = 10^{-3}$ mol/dm³; $[\text{MMA}]$ varies from 0.0468 to 0.1404 mol dm⁻³; (b) KPS order: $[\text{MMA}] = 0.0936$ mol dm⁻³, $[\text{FAS}] = 10^{-3}$ mol/dm³; $[\text{KPS}]$ varies from 2.5×10^{-4} to 1×10^{-3} mol/dm³; (c) FAS order: $[\text{MMA}] = 0.0936$, $[\text{KPS}] = 10^{-3}$, $[\text{FAS}]$ varies from 2.5×10^{-5} to 1.5×10^{-3} mol/dm³.

Eq. (16),

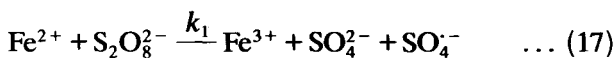
$$V_p'(\text{experimental}) \propto [M]_w^{1.50} [S_2O_8^{2-}]_w^{0.42} [Fe^{2+}]^x \quad \dots (16)$$

At 40°C, the order plot of Fe^{2+} is a curved line, $x=0.5$ when $r = ([FAS]/[KPS])$ is 0.025, and $x=0$ when $r = 1.0$. for a given KPS concentration, equivalent amount of Fe^{2+} ions would disappear via reaction (1), and the excess Fe^{2+} ions would accelerate reaction (2) which would lower the polymerization rates. It is found that the conventional order plot of Fe^{2+} ions in the FAS-vinyl acetate-KPS system²¹ is a curved line at 30°C. When r is very low (about 0.01), the order of FAS is about 0.50, but the order becomes negative if $r > 2.0$.

At 10°C, the latex is a milky white precipitate, while at 40°C it is a very stable yellow colloid (Table 1), possibly due to the adsorption of positively charged aquo hydroxy ferric ion complexes formed *in situ*, which are believed to act as peptisers²². The order (0.42) of KPS at 40°C indicates that the kinetics here probably follows the Smith-Ewart type model of emulsion polymerization¹⁻², where initiation and termination in the positively charged latex particles would take place due to the absorption of negatively charged primary radicals ($SO_4^{\cdot -}$). The colloid stability (CS) of the latex solution was found to increase with temperature (Table 1), possibly due to the higher concentrations of peptisers (i.e. ferric ion complexes)²⁰.

In the KPS-MMA-FAS system, the latex particles are negatively charged due to sulphate end groups¹⁻². After continuous adsorption of positively charged complex ferric ions, there will be charge reversal on the particles^{14,23-25}, when the polymer passes into the colloidal state above 20°C.

It was noted that NaF decreased the initial rates of polymerizations (Table 1). It seems that NaF increased the ionic strength (μ) of the medium and hence decreased the rate constant k_1 of the ionic reaction³, viz.



and also the number of latex particles per ml (N) through incipient coagulation, as indicated by the decrease of CS of the latex solutions (Table 1).

At lower temperature (10°C or less), there was no measurable change in pH of the solution during the reactions, and so the reactions (9) to (11)

would not be important under the experimental conditions. Since the polymer was a milky white precipitate, it indicates that no coloured complexes of Fe^{3+} ions were produced in measurable quantities, and the colloidal polymer was coagulated by the hydrated Fe^{2+} and Fe^{3+} ions. In the Fenton's reagent initiated system (Fe^{2+} -MMA- H_2O_2 - H_3PO_4), the polymer produced was always a precipitate at all temperatures, white precipitate at 4 to 10°C and yellow one above 10°C. Since the polymers are known to have OH end groups²⁶⁻²⁸, they cannot adsorb positively charged ferric ion complexes through electrostatic interactions. The yellow colour of the polymers at higher temperatures was due to the physical adsorption of coloured ferric ion complexes. This yellow colour of the freshly prepared polymer could be washed out with NaF solution or with dilute HCl. The polymer after thorough washing, remains apparently white after vacuum drying at 50°C. Under similar conditions, the polymer from the FAS-MMA-KPS system becomes yellow.

Table 2 shows the amount of iron present per g of purified and dried polymer. It is found that the amount of iron per g of polymer from the FAS-MMA-KPS system at a given temperature is always higher than that in the polymer from the FAS-MMA- H_2O_2 system. Further in any redox system, the iron content of the polymer is more at higher temperatures, possibly due to higher concentrations of aquo hydroxy ferric ion complexes²⁰. It is suggested that the negatively charged sulphate end groups of the polymers from the FAS-MMA-KPS system might retain a large amount of ferric ion complexes through electrostatic interactions.

Table 2—Amount of iron present (in grams) per gram of purified polymer (Polymethyl methacrylate)

System A: $[FAS] = [KPS] = 10^{-3} \text{ mol dm}^{-3}$, $[MMA] = 9.36 \times 10^{-2} \text{ mol dm}^{-3}$.			
System B: $[H_2O_2] = [FAS] = 10^{-3} \text{ mol dm}^{-3}$, $[MMA] = 9.36 \times 10^{-2} \text{ mol dm}^{-3}$.			
† H_2O_2 contains phosphoric acid as stabiliser.			
System	Temp. °C	Nature of latex particles	g of Fe/g of polymer
A	40	Yellow colloid	4.56×10^{-3}
A	10	White precipitate	3.52×10^{-3}
B	40	Very light yellow precipitate	1.19×10^{-4}
† (pH = 3.35)			
B	10	White precipitate	4.04×10^{-5}
† (pH = 3.40)			

Figure 4 shows the time average rates of polymerizations and colloidal stability (CS) of the latex solutions as function of temperature. The increase in CS is probably associated with the increase in peptiser concentrations with temperature, while the rates of polymerizations decrease possibly due to faster rates of the reaction (2) with temperature rise.

In Fig. 1, it is seen that the initial rates of polymerizations (R_1) in the FAS-MMA-KPS system are higher than those (R_{1a}) in the FAS-MMA-H₂O₂-H₃PO₄ system under almost identical experimental conditions, although the reactivity of OH radicals with respect to MMA in aqueous solutions, is about 10 times higher than that of SO₄⁻ radicals²⁹.

$$R_1/R_{1a} \text{ (from Fig. 1) =}$$

$$= \frac{\text{yield of polymer in 5 min (Fig. 1D)}}{\text{yield of polymer in 5 min (Fig. 1B)}}$$

$$= 4.5 \text{ at } 10^\circ\text{C, and}$$

$$R_1/R_{1a} = \frac{\text{yield of polymer in 10 min (Fig. 1C)}}{\text{yield of polymer in 10 min (Fig. 1A)}}$$

$$= 4.4 \text{ at } 40^\circ\text{C,}$$

$$\text{where as, } (k_1/k_{1a}) =$$

$$= \frac{10^{11} \exp(-12100/1.987T) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}{4.45 \times 10^8 \exp(-9400/1.987T) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

$$= 1.85 \text{ at } 10^\circ\text{C, and } 2.93 \text{ at } 40^\circ\text{C.}$$

where k_{1a} is the rate constant of the reaction

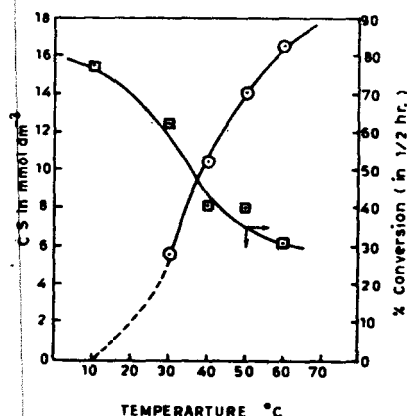
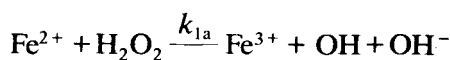


Fig. 4—Colloid stability (CS) as a function of temperature and also per cent conversion in (1/2)h as a function of temperature: ○ CS and □ per cent conversion. [MMA] = 0.0936 mol dm⁻³, [KPS] = [FAS] = 10⁻³ mol/dm³; temperature varies.



The system, Fe²⁺-H₂O₂, is very complex³⁰ compared to Fe²⁺-S₂O₈²⁻ system³. Under identical experimental conditions, the stationary concentration of ·OH radicals in the FAS-MMA-H₂O₂ system is much less than that of SO₄⁻ radicals in the FAS-MMA-KPS^{1-3,30}. Higher values of k_1 and of primary radical concentrations (SO₄⁻) are probably responsible for the higher rates of polymerizations in the latter.

Figure 1 and Table 1 show that the rates of polymerizations decreased with the rise in temperature possibly due to the higher rate of (2) compared to that of (3)¹⁻⁵ (Fig. 4). In the absence of NaF, (CS) of the latex solution and its conductance increased with the rise in temperature (Table 1 and Fig. 2), but pH decreased possibly due to the reactions (9) to (11) where the peptiser viz. the aquohydroxy ferric ion complexes, and H⁺ ions, were produced. The higher the temperature, the greater would be the concentration of the peptiser and of H⁺ ions^{18,19}. This means that (CS) and conductance of the latex solution would increase with temperature but pH would decrease. This is consistent with the results shown in Table 1 and Fig. 4.

In the presence of NaF, the reactions (9) and (11) would not take place, and so (CS) would decrease and pH change (i.e. ΔpH) would be zero (Table 1). Since the latex solution was colourless, it supports the idea that colourless complexes of Fe³⁺ ions such as (FeF)²⁺, (FeF₂)⁺ etc. were formed in the presence of F⁻ ions¹⁸, and no coloured aquo hydroxy ferric ion complexes were formed. In the absence of this coloured complex and in the presence of Na⁺ ions, the (CS) value would decrease (Table 1). The added Na⁺ ions would obviously alter the conductance of the solution (Table 1).

In the Fe²⁺-MMA-H₂O₂-H₃PO₄ system, the Fe³⁺ ions produced, would be complexed by the phosphate ions, as a result of which reactions (9) to (11) and would not occur; pH and conductance would not change (Table 1). ($\bar{M}_n$) of polymers was found to decrease with the rise in temperature (Table 1), which is consistent with the theories of the heterogeneous aqueous polymerizations initiated by free radicals¹⁻².

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