

Nonconventional Emulsion Polymerization of Methyl Methacrylate. Effect of Cu(II)/Histidine Complex Catalyst and Different Peroxo-Salts

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ABSTRACT: The characteristics of nonconventional (soap-free) aqueous emulsion polymerization reactions of methyl methacrylate were evaluated by the catalytic effect of *in situ* developed different transition metal (II) chelate complex with amino acids initiated by different peroxy salts like potassium monopersulfate (KMPS, KHSO_5), potassium persulfate (KPS, $\text{K}_2\text{S}_2\text{O}_8$), ammonium persulfate (APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$). From the comparative data, the CuSO_4 /histidine chelate complex was selected as a novel catalyst for a detailed kinetic and spectrometric study of polymerization. Both kinetic and thermodynamic aspects of the polymerization dictate which initiator and particle morphology are obtained. The complex catalyzed polymerization proceeded smoothly until high conversion and yielded stable emulsions. The apparent activation energies (E_a) for the complex catalyzed emulsion polymerization were computed for different initiators to be 34, 38, and 46 kJ mol^{-1} , each a very low value. Use of these values and activation energies of propagation and termination for MMA gave an unexpectedly low activation energies (E_d , 26, 34, and 51 kJ mol^{-1} for KMPS, KPS, and APS respectively) to the decomposition of different persulfate initiators in the complex catalyzed system. The emulsion polymer latex was characterized through the determination of average molecular weights of the purified polymers by gel permeation chromatography (GPC) and viscosity methods and the morphology by scanning electron microscopy (SEM). The coordination complex catalytic system shows excellent industrial performance characteristics in preparing micro- to nano-scale latex particles.

KEY WORDS Complex Catalysis / Soap-Free Emulsion / Kinetics / Micro-Particles / Scanning Electron Microscopy (SEM) /

In recent years number of papers have been published on emulsion polymerization of vinyl monomers using persulfates as initiators.^{1–5} Also several studies were done in the emulsion polymerization of vinyl monomers using different redox pair initiation systems.^{6–13} However the use of these initiation systems were not straight forward and often leads to low conversion of monomers to polymer in oxygen-free (inert) atmosphere. Again most of these processes were carried out at high temperatures, but none of these functioned suitably for commercial purpose.

In our different publications we have reported the emulsifier-free emulsion polymerization of acrylonitrile initiated by potassium monopersulfate together with *in situ* developed complex initiating systems, such as Cu(II)/Glycine¹⁴ and Cu(II)/ H_2 Salen¹⁵ with comparison of results of N_2 atmosphere with that of the O_2 atmosphere in order to design a simple low-cost polymerization technique.

The present work attempts the study on the soap-free emulsion polymerization of MMA with novel catalytic action of *in situ* developed complex of Cu(II) salts with a series of water soluble amino acids initiated by three peroxy salts and describes the kinetic

results and the morphology of particles observed with Cu(II)/histidine/persulfates initiated systems.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) monomer (BDH) was purified as reported earlier.³ Potassium monopersulfate (KMPS, KHSO_5) was a gift sample from Du pont Co. USA and was used as received. Potassium persulfate (KPS, $\text{K}_2\text{S}_2\text{O}_8$) and ammonium persulfate (APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$) were analR grade, BDH chemicals Ltd, Poole, UK. Amino acids (E-Merck) were used as such. All other reagents were of BDH (AR) grade and used after purification. All water used was purified by double distillation.

Polymerization Method

Batch emulsion polymerization experiments were carried out in a round bottom flask containing known concentrations of monomer (MMA), CuSO_4 and amino acids under nitrogen atmosphere. The solution was stirred at 400–600 rpm. The speed is in the range where the agitation has no remarkable effect on the rate of the

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Table I. Variation of % conversion in MMA polymerization under catalytic influence of various metal (II) salts, amino acids and M(II)/amino acid couple initiation at 50 °C

Amino Acids	No Salt			Cu(II)SO ₄			Co(II)SO ₄			Ni(II) Cl ₂			M _n (II)(OAc) ₂		
	KMPS	KPS	APS	KMPS	KPS	APS	KMPS	KPS	APS	KMPS	KPS	APS	KMPS	KPS	APS
No amino acid	6.0	5.4	4.8	8.5	7.3	6.2	8.1	7.2	6.0	7.8	7.1	5.9	6.8	6.5	6.2
Alanine	8.2	8.1	7.9	29.4	28.4	26.4	27.4	26.5	25.1	26.8	25.4	24.5	25.4	22.4	21.6
Aspartic acid	6.8	6.4	6.2	25.9	24.5	22.4	23.4	21.2	20.8	19.2	18.1	16.5	21.4	20.2	18.1
Glutamic acid	6.2	6.0	5.8	28.4	27.4	26.2	27.2	26.5	25.1	26.7	25.8	24.1	18.6	18.2	16.5
Glycine	8.3	8.1	8.0	30.6	28.1	27.5	28.4	26.5	24.5	26.1	24.0	22.5	25.8	23.4	20.8
Histidine	8.5	8.2	8.0	33.09	29.5	23.6	30.4	27.4	21.4	28.4	26.1	20.4	27.7	25.5	18.4
Lysine	6.1	5.8	5.4	26.4	24.8	22.2	22.8	20.4	18.5	21.7	20.4	18.4	19.4	18.6	16.8
Serine	7.4	7.2	6.8	21.6	20.4	18.5	20.1	18.5	17.4	18.4	16.5	15.4	20.5	11.5	10.2
Theonine	5.8	5.7	4.6	23.4	22.2	21.5	22.4	20.2	18.4	20.4	19.2	18.1	18.4	16.2	14.5

[M(II)] = 10.0 × 10⁻³ mol dm⁻³, [Amino acid] = 10.0 × 10⁻³ mol dm⁻³, [KMPS] = 12.9 × 10⁻³ mol dm⁻³, [KPS] = 10.0 × 10⁻³ mol dm⁻³, [APS] = 10.0 × 10⁻³ mol dm⁻³.

Table II. Variation of % conversion in MMA polymerization with different Cu(II) salts and various amino acids in different persulfate initiators at 50 °C

Amino Acids	CuSO ₄			CuCl ₂			Cu(OAc) ₂			Cu(NO ₃) ₂		
	KMPS	KPS	APS	KMPS	KPS	APS	KMPS	KPS	APS	KMPS	KPS	APS
No amino acid	8.5	7.3	6.2	8.3	7.3	6.1	7.9	7.8	5.9	8.2	7.8	6.2
Alanine	27.4	25.4	22.4	25.5	24.5	19.4	26.4	26.5	20.0	26.4	22.8	20.0
Aspartic acid	25.2	23.8	21.5	25.0	23.6	21.4	26.5	25.0	21.2	25.4	24.8	20.6
Glutamic acid	26.5	25.4	24.2	24.5	23.2	20.8	28.4	27.5	21.3	26.5	24.2	18.2
Glycine	28.4	27.5	25.4	27.8	26.4	20.4	28.8	28.4	22.0	27.4	25.5	20.8
Histidine	33.09	29.5	23.6	31.4	28.5	23.0	30.4	28.0	22.8	29.5	27.4	21.4
Lysine	26.5	24.4	20.2	25.2	23.8	19.2	25.6	24.2	20.2	25.4	22.8	20.2
Serine	25.5	23.2	22.5	23.4	24.5	19.5	26.4	25.7	20.8	25.5	23.5	19.8
Theonine	27.3	26.5	23.4	26.4	25.5	21.0	29.5	28.4	21.6	28.4	25.2	19.5

[Cu(II)] = 10.0 × 10⁻³ mol dm⁻³, [Amino acid] = 10.0 × 10⁻³ mol dm⁻³, [KMPS] = 12.9 × 10⁻³ mol dm⁻³, [KPS] = 10.0 × 10⁻³ mol dm⁻³, [APS] = 10.0 × 10⁻³ mol dm⁻³, [MMA] = 0.983 mol dm⁻³.

polymerization. A requisite amount of specific initiator from stock solution was carefully injected to the vessel. It was found that the agitation produces dispersion of insoluble monomer in the continuous phase. The reaction is terminated by keeping the flask in ice-cold water and by addition of a known excess of ferrous ammonium sulfate that spontaneously consumed unreacted initiator.⁴ The precipitated polymers were filtered and washed repeatedly with water and absolute alcohol and dried to constant weight at 60 °C. The % conversion and rate of polymerization were calculated gravimetrically.

Polymer and Latex Characterization

The number average molecular weight (M_n) of the purified polymer is determined by gel permeation chromatography (GPC) and the viscosity average molecular weight (M_v) of the purified polymer is determined in acetone at 30 °C by Ubbelohde viscometer using the following equation:¹⁶ $[\eta] = 7.7 \times 10^{-5} M_v^{0.7}$.

The visible spectra of Cu(II) and Cu(II)/Histidine complex with monomer (MMA) and initiators were recorded in a PerkinElmer UV-Vis Spectrophotometer. The morphology of the PMMA latex was studied by a Joel Ltd, Japan, Model No. 5200 Scanning Electron

Microscopy.

RESULTS AND DISCUSSION

The results on study of emulsion polymerization of methyl methacrylate initiated by different persulfate initiators such as KHSO₅, K₂S₂O₈, and (NH₄)₂S₂O₈ with the catalytic action of *in situ* developed different transition metal salts/amino acids complex, Cu(II) salts/amino acid complex, and Cu(II)SO₄/histidine complex are listed in Table I, II, and III respectively. The possibility of Cu(II)/ amino acids couple initiating polymerization was excluded by the fact that no polymer was precipitated with Cu(II)/amino acid couples in absence of peroxy salts, even after 48 h.

It is quite clear that addition of amino acids to CuSO₄ solution activates the rate of initiation of polymerization with all the three initiators, KMPS, KPS, and APS. Further from Tables I and II, it is evident that CuSO₄/histidine *in situ* developed new catalytic system displayed a quite high activity on the rate of decomposition of initiator and polymerization (R_p). Again among the three initiators, KMPS gives high R_p value as compared to KPS and APS in presence of Cu(II)/histidine

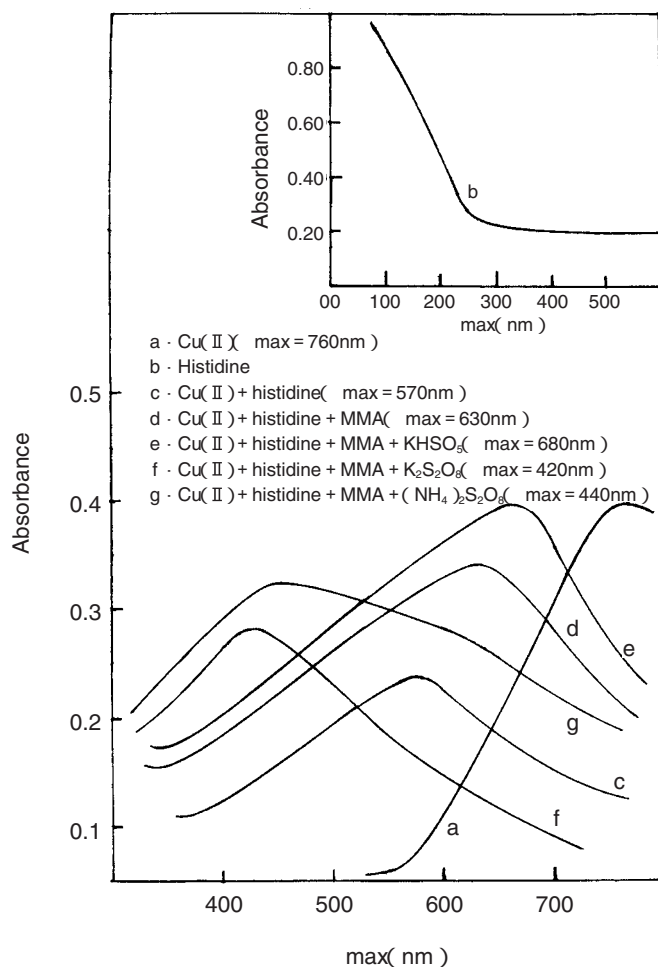
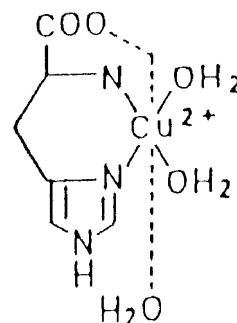


Figure 1. Spectral evidence for the interaction of Cu(II) with histidine, MMA, KMPS, KPS, and APS at $[CuSO_4] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[Histidine] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[MMA] = 0.983 \text{ mol dm}^{-3}$, $[KMPS] = 12.9 \times 10^{-3} \text{ mol dm}^{-3}$, $[KPS] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, and $[APS] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$ (a) $CuSO_4$ (b) histidine, (c) $CuSO_4$ + histidine, (d) $CuSO_4$ + histidine + MMA, (e) $CuSO_4$ + histidine + MMA + KMPS, (f) $CuSO_4$ + histidine + MMA + KPS, and (g) $CuSO_4$ + histidine + MMA + APS.

complex.

Figure 1 shows the visible spectra of various mixtures like $Cu(II)SO_4$, $Cu(II)/Histidine$, $Cu(II)/Histidine/MMA$, $Cu(II)/Histidine/MMA/KMPS$, $Cu(II)/Histidine/MMA/KPS$, and $Cu(II)/Histidine/MMA/APS$ measured to obtain complete picture of the interaction between the reacting components and their relationship with the rate data. The tridentate ligand character of amino acids in conjunction with colored cations like $Cu(II)$ to form a complex in an acidic medium (pH = 2.7) is well recognized^{17–19} and in case of copper-histidyl complexes in aqueous solution, the involvement of imidazole nucleus in coordination with copper along with their stability constants has been reported^{20,21} as per the structure in Scheme 1. The ML type structure of the complex was established from the proportionalities obtained from the rate equation, *i.e.*,



Scheme 1. Cu–Histidine ML-Complex.

$Cu(II)$: Histidine as 1:1 with stability constant $\log k$ 10.25. This type of imidazolyl group coordination is different from glycine type coordination.²⁰ The imidazolyl group reduces the redox potential of $Cu(II)$ -species as evidenced from the increase in R_p by reducing the free-radical scavenger nature of the transitional metal ions,⁴ $Cu(II)$. Further the stability constants of $Cu(II)$ -glycine and $Cu(II)$ -imidazole complexes are found to be $\log k$, 0.48 and $\log k$, 2.9 respectively. On the basis of the above findings, the authors thought $Cu(II)$ -histidine to work better over $Cu(II)$ -glycine complex already reported by us¹⁴ in catalyzing the polymerization reaction.

The high % conversion and R_p values with $Cu(II)/histidine$ couple may probably be due to the high rate of production of initiating radicals by the homolysis of the initiator bound by the transient complex of $Cu(II)/histidine$ where the internal energy is transferred to the initiators. A comparative high rate of polymerization with KMPS may be ascribed to the production of more and different initiating radicals like OH^\bullet , $SO_4^{\bullet-}$, HSO_4^\bullet , HSO_3^\bullet in comparison to the single type radical $SO_4^{\bullet-}$ formed from KPS and APS. The formation of these primary radicals are evidenced by electron spin resonance (ESR) spectra and end-group analysis of the purified polymers according to the methods of Palit²² and Saha *et al.*²³ Thus these primary radicals start chain growth in microdroplets or aqueous phase.

Also, the effect of the catalyst $Cu(II)/histidine$ concentration on the stability of MMA–water emulsion was studied as shown in Table III. It is indicated that the stability of MMA–water emulsion increased by the introduction of $Cu(II)/histidine$ into the emulsion medium containing the water soluble initiators. A representative SEM photograph (Figure 2) of the polymer latex (Table IV) illustrated that by controlling the monomer conversion profile with $Cu(II)/histidine$ complex, monodispersed latex particles with structures ranging from microdomain to hollow are possible. Figure 3 shows the presence of cavities and voids on the fracture surfaces of the polymer latex, a characteristic

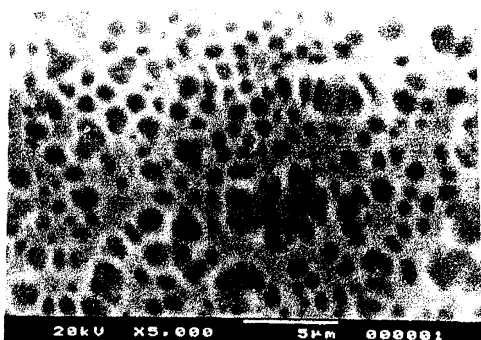
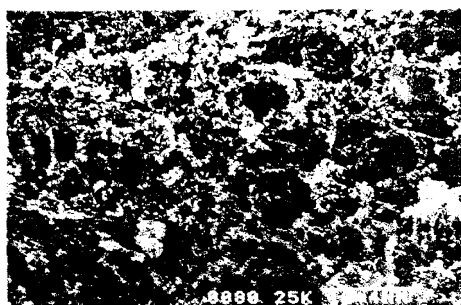
Table III. Effect of monomer concentration on % conversion and molecular weight, M_v , M_n of PMMA at 50 °C

[MMA] mol dm ⁻³	% Conversion			Molecular Weight					
	KMPS	KPS	APS	$M_v \times 10^{-4}$			$M_n \times 10^{-4}$		
				KMPS	KPS	APS	KMPS	KPS	APS
0.983	30.9	28.3	25.8	2.8	0.9	0.7	2.3	0.8	0.6
1.484	33.0	29.5	23.5	3.3	1.9	1.7	3.1	1.7	1.6
1.976	64.4	56.9	45.9	6.2	5.6	5.2	5.8	5.4	4.9
2.467	68.3	60.5	52.1	8.7	8.6	6.2	7.3	8.5	6.0
2.959	65.9	59.7	54.3	9.2	9.0	8.2	8.5	8.4	8.1

[Cu(II)SO₄] = 10.0 × 10⁻³ mol dm⁻³, [Histidine] = 10.0 × 10⁻³ mol dm⁻³, [KMPS] = 12.9 × 10⁻³ mol dm⁻³, [KPS] = 10.0 × 10⁻³ mol dm⁻³, [APS] = 10.0 × 10⁻³ mol dm⁻³.

Table IV. Variation of particle size in MMA polymerization with monomer conversion in different persulfate initiators at 50 °C for 3 h

MMA mol dm ⁻³	% Conversion			Av. diameter of latex particles, nm		
	KMPS	KPS	APS	KMPS	KPS	APS
0.983	30.9	28.3	25.8	33	38	35
1.484	33.0	29.5	23.5	38	72	31
1.976	64.4	56.9	45.9	62	53	46
2.467	68.3	60.5	52.1	64	58	48
2.959	65.9	59.7	54.3	62	57	51

**Figure 2.** SEM Photograph of powder PMMA polymer latex sample.**Figure 3.** SEM photographs of the fracture surface of the polymer latex showing cavities and voids.

of emulsion polymerization.²⁴ The electron micrograph data reveal that the particle size of the PMMA emulsion latex is less than 100 nm. This small particle size of PMMA may be attributed to the retardation in particle growth. Similar results of smaller particle size and retardation in particle growth were reported by Capek *et al.*²⁵ in the microemulsion polymerization of butyl acrylate in presence of radical scavenger. Thus, complex catalyzed emulsifier-free emulsion polymerization

can hopefully be utilized to prepare nanoscale latex particles.

Further, in the non-conventional emulsion polymerization experiments, the concentrations of the reaction components were varied to establish the relationship between the catalyzed influence and mole-ratios of the donor-acceptor entities.

Variation of [Monomer]

Variation in monomer (MMA) concentration from 0.983 to 2.9 mol dm⁻³ shows that the rate of polymerization and the maximum conversion are found to increase for all the three initiators as shown in Table III. The increase may be due to the availability of larger number of monomer molecules in propagation step that results consequently in observed findings.

From the double logarithmic plot of R_p vs. [MMA], the order of reaction with respect to monomer has been calculated to be 0.54 for KMPS, 0.69 for KPS, and 0.65 for APS system. These values are less than unity as expected for ideal kinetics. Less than one value of order has also been cited in the literature as Chapiro²⁶ found the monomer exponent varying from one to less than one and the findings were attributed to the presence of impurity in the polymerization system. In addition, the deviation from unity is normally observed as the polymerization system becomes heterogeneous in nature.²⁷

The molecular weights M_v and M_n of the PMMA samples determined by viscosity and GPC methods are found to increase 2.8 × 10⁴~9.2 × 10⁴ and 2.3 × 10⁴~8.5 × 10⁴ respectively with increasing [MMA] from 0.983 to 2.9 mol dm⁻³ for KMPS initiator system, and there is slight variation in molecular weight values

for other initiators as shown in Table III.

Variation of $[CuSO_4]$

The effect of $[CuSO_4]$, $0.5 \times 10^{-2} \sim 2.5 \times 10^{-2} \text{ mol dm}^{-3}$, on the rate and conversion percent was studied resulting in determining the mole-ratios of the $CuSO_4$ to histidine in forming the complex catalyst. The maximum conversion and R_p increase with increase in $[CuSO_4]$ from $0.5 \times 10^{-2} \sim 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ in the range 13.7–79.2%, 10.3–68.9%, and 5.7–64.3% for KMPS, KPS, and APS respectively and then decrease for all three initiators. The increase in initial rate may be due to the increasing catalysis since an appropriate mole ratio of Cu(II) to histidine is solution favors the formation of activated complex which actively interacts with the peroxo-bridge orbital, resulting in the rupture of O–O bond in a sequential fashion. The decrease in the rate may be due to the retardation effect of the transition metal ions, *i.e.*, excess Cu(II) ion. From the double logarithmic plots, the orders with respect to Cu(II) ion were found to be 0.89 for KMPS, 1.0 for both KPS, and APS.

Variation of $[Histidine]$

The effect of histidine as one of the components in complex catalyst initiating system has been studied by varying $[histidine]$ in the range, $0.5 \times 10^{-2} \sim 2.5 \times 10^{-2} \text{ mol dm}^{-3}$. The initial rate and the percentage conversion are found to increase in the range 26.4–66.6%, 20.6–60.9%, and 12.6–60.8% for KMPS, KPS, and APS respectively. From the double logarithmic plot of R_p with $[histidine]$, the orders were observed to be 0.84, 0.9, and 1.0 for KMPS, KPS, and APS respectively.

It may be interpreted that the catalytic activity of Cu(II) in cleaving the peroxo bond is enhanced by coupling with the chelating histidine molecule where a competitive coordination between Cu(II) ion, peroxo initiators and histidine takes place. This is further supported from the spectral absorbance of the complex with the three initiators (Figure 1). Due to the competition, the stability of the Cu(II)/histidine complex is distorted towards Cu(II)-peroxo salts interaction and the internal energy of the complex is released in the direction of the peroxo bond, resulting in its cleavage. As the curve e with KMPS is quite different from the curves f with KPS and g with APS, the more interaction of KMPS with the complex resulted in highest initiation activity although all these peroxo salts showed high activity.

Variation of $[Initiators]$

The effect of $[initiator]$ on R_p and maximum conver-

sion has been studied by varying their concentration in the range, $0.5 \times 10^{-2} \sim 2.5 \times 10^{-2} \text{ mol dm}^{-3}$ for KPS and APS and $0.64 \times 10^{-2} \sim 3.22 \times 10^{-2} \text{ mol dm}^{-3}$ for KMPS. It is observed that with increase in the concentrations of three initiators, the maximum conversion increase in the range 22.9–73.5%, 18.3–65.4%, and 13.7–58.6% for KMPS, KPS, and APS respectively. Plots of $\log R_p$ vs. $\log [Initiators]$ indicate the overall rate to be 0.92, 0.88, and 1.0 order dependent on KMPS, KPS, and APS concentrations respectively.

This deviation from the normal half order dependence in conventional free radical polymerization may be interpreted as the complexation of the initiator with Cu(II) ion in the Cu(II)/histidine complex resulting in selective stereo-chemical initiation involving in a *cis*-attack on the bound monomer in a similar manner as seen in the polymerization system.²⁸ Cu(II)/ α -naphthol/KHSO₅/AN/H₂O. From the results, it has been seen that between three peroxo initiators, KMPS is the most effective initiator increasing both rate and percentage conversion which may be ascribed to the formation of different types of initiating free-radicals as shown in the mechanism.

Variation of Solvents

The addition of 20% (v/v) water miscible organic solvents such as acetic acid, acetone, methanol, and DMSO to the reaction medium retarded the initial rate and maximum conversion. The results obtained clearly show the decreasing order of initial rate and % conversion as follows: DMSO (negligible) < acetone (42.3%, 38.5%, and 36.7%) < acetic acid (55.2%, 51.4%, and 49.8%) < methanol (60.3%, 55.8%, and 51.3% for KMPS, KPS, and APS, respectively). The retardation or depression by these solvents may be due to (i) solvation of Cu(II) ions lessening complex forming ability, (ii) simultaneous oxidation of the additives by initiators, thus reducing the optimum concentration of the initiating radicals in the immediate vicinity of the monomer. The oxidation of compounds such as ethyl alcohol to ethyl acetate and acetic acid to glycolic acid has been established,²⁹ (iii) premature termination resulting from activity transfer to these solvents.

Temperature Dependence

The effect of temperature in the polymerization medium on the initial rate and % conversion has been investigated varying the temperature in the range 40–70 °C. The results show with increase temperature both R_p and % conversion increase for all the three initiators. The overall activation energies (E_a) of polymerization were calculated from the Arrhenius plots of $\log R_p$ vs. $1/T$ (Figure 4) to be 34, 38, and 46 kJ mol⁻¹ for KMPS,

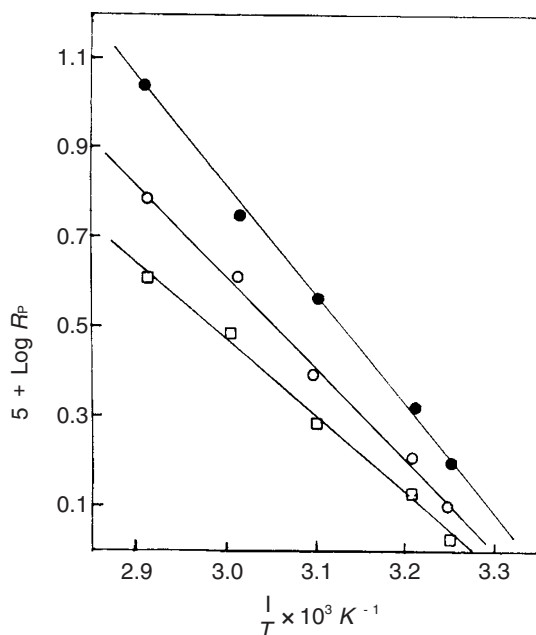


Figure 4. Arrhenius plot of $\log R_p$ vs. $1/T$ at $[\text{Cu(II)}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{Histidine}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{MMA}] = 0.993 \text{ mol dm}^{-3}$, $[\text{KMPS}] = 12.9 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{KPS}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{APS}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, (●) KMPS, (○) KPS, and (□) APS.

KPS, and APS respectively. E_a is related to the activation energy of initiator decomposition (E_d), propagation (E_p) and termination (E_t) by the equation:

$$E_a = E_p + (E_d - E_t)/2$$

Substituting in the values $E_p = 29$ and $E_t = 16 \text{ kJ mol}^{-1}$ respectively for MMA³⁰ and $E_a = 34, 38,$ and 46 kJ mol^{-1} (Figure 4), $E_d = 26, 34,$ and 51 kJ mol^{-1} was estimated for KMPS, KPS, and APS respectively in the present polymerization. These E_d values are much lower than reported for *t*-butyl perpivalate (113 kJ mol^{-1}).³¹ Figure 5 shows the relationship between R_p with the reciprocal of DP of PMMA when the initiators (KMPS, KPS, and APS) concentrations were varied at 50°C . Linear relationships observed for all initiators exclude any significant chain transfer to the initiator in the present systems. This is in accordance with the fact that dialkyl fumarate is not incorporated in the resulting polymers in the copolymerization with MMA.³² Further, the micelle number in the present system is determined to be 2.3×10^{17} against the theoretical values³³ of 10^{18} characteristic of emulsifier-free emulsion polymerization.

Variation of Time

Figure 6 shows the plot between the time of reaction and percentage conversion. The reaction was carried out at 50°C for the three initiators, keeping the concentrations of MMA, Cu–histidine constant. It was observed that for all the three initiators upto 180 min of

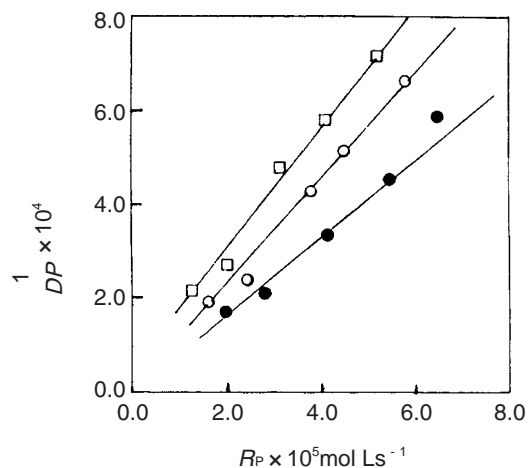


Figure 5. Dependence of degree of polymerization (DP) of MMA on the polymerization rate (R_p) at 50°C . (●) KMPS, (○) KPS, and (□) APS.

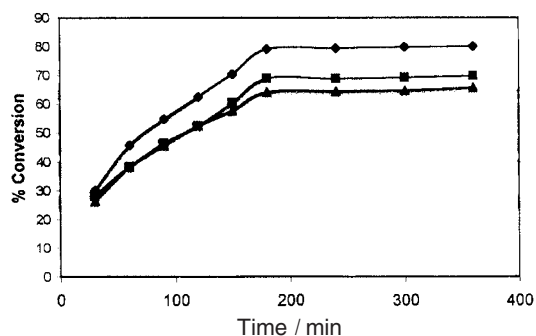


Figure 6. Time vs. % conversion curves for the polymerization of MMA at 50°C with $[\text{Cu(II)}] = 20.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{Histidine}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{MMA}] = 0.983 \text{ mol dm}^{-3}$, for different initiators: (●) $[\text{KMPS}] = 12.9 \times 10^{-3} \text{ mol dm}^{-3}$, (○) $[\text{KPS}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, (□) $[\text{APS}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$.

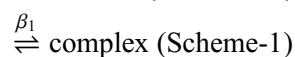
reaction, polymerization showed a dead end polymerization tendency, *i.e.*, the initiation activity of the initiator is high at initial period and decreases towards the end.

Mechanism

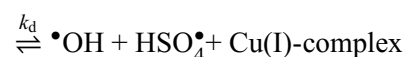
The mode of initiator decomposition and the chain initiation and termination mechanism of polymerization involving the novel catalytic system Cu(II)/histidine/persulfates can be interpreted as follows:

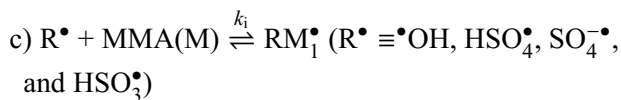
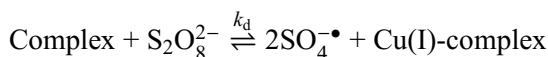
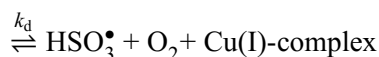
1. Chain initiation by Cu(II)/histidine complex catalysis:

a) $\text{Cu(II)} + \text{Histidine (amino acid)}$



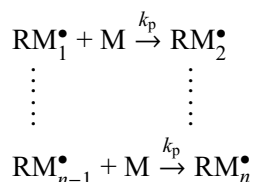
b) $\text{Complex} + \text{HSO}_5^- \xrightarrow{k_d} \text{SO}_4^{\bullet-} + \text{H}_2\text{O} + \text{Cu(I)-complex}$



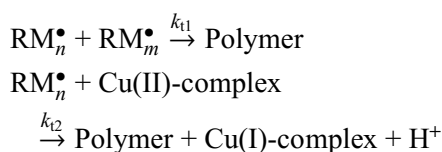


Formations of these primary radicals are discussed earlier in results and discussion section.

2. Propagation:



3. Termination:



Applying the steady state principle and assuming mutual termination the rate expression is observed as follows:

$$\begin{array}{l} R_p \propto [\text{Cu(II)}]^{0.89} [\text{Histidine}]^{0.84} [\text{KMPS}]^{0.92} [\text{MMA}]^{0.54} \\ R_p \propto [\text{Cu(II)}]^{1.0} [\text{Histidine}]^{0.9} [\text{KPS}]^{0.88} [\text{MMA}]^{0.69} \\ R_p \propto [\text{Cu(II)}]^{1.0} [\text{Histidine}]^{1.0} [\text{APS}]^{1.0} [\text{MMA}]^{0.65} \end{array}$$

CONCLUSIONS

The most interesting and significant outcome of the paper is the conversion of the inhibitors/retarders (transition metal ions) into accelerator of polymerization catalyzed by the *in situ* developed high activity coordination complex of Cu(II)/histidine. The novel non-conventional complex initiating system is very efficient in promoting the decomposition rate of the initiator, the polymerization rate and also leads to stabilize the emulsion latex to high conversion in absence of an added emulsifier. The polymer latexes were characterized by determining molecular weight by viscosity & GPC methods and their microdomain to hollow structure was shown by SEM. The detailed kinetic parameters and variables for all the three initiator systems are determined and discussed. Out of the three initiators used, KMPS is found to be most effective in enhancing the % conversion and the rate of the polymerization and their initiation activities are in the order: KMPS > KPS > APS. Further, nanoscale latex particles could be obtained in the nonconventional emulsion polymerization. Hence it is a promising technique for preparation

of polymer nanoparticles and nanocomposites that are to be reported further from this laboratory.

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