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Synthesis and kinetic studies of PMMA nanoparticles by non-conventionally initiated emulsion polymerization

Prafulla K. Sahoo *, Roomky Mohapatra

Department of Chemistry, Utkal University, Vani Vihar, Bhubaneswar 751 004, India

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Abstract

The aqueous emulsifier-free emulsion polymerization of methyl methacrylate (MMA) was studied under the catalytic effect of in situ developed bivalent transition metal-EDTA complex with ammonium persulfate (APS, $(NH_4)_2S_2O_8$) as initiator. Out of these, Cu(II)-EDTA system was selected for detailed kinetic and spectrometric study of polymerization. The apparent activation energy E_a, 34.5 kJ/mol, activation energy of initiator decomposition E_d, 26.9 kJ/mol, energy of propagation E_p, 29 kJ/mol and energy of termination E_t, 16 kJ/mol were reported. The emulsion polymer (PMMA) latex was characterized through the determination of the size and morphology by scanning electron microscopy, the average molecular weight by GPC and viscosity methods and the sound velocity by ultrasonic interferometer. From the kinetic results, the rate of polymerization, R_p at 50 °C was expressed by

$$R_p = K[\mathrm{Cu(II)}]^{0.35}[\mathrm{EDTA}]^{0.69}[\mathrm{APS}]^{0.57}[\mathrm{MMA}]^{0.75}$$

Keywords: Non-conventional emulsion; Complex catalyst; Kinetics; Nanoparticles; Ultrasonic velocity

1. Introduction

There has been some intense research on emulsifier-free emulsion polymerization of vinyl and acrylic monomers using persulfates as initiators [1–10] and complex catalyzing systems for their application in the biomedical field and as magnetic materials, coatings or as adhesives. This process has been used in predicting the morphology of latex particles [11]. Formation of the particles (nucleation) and their analysis are possible, keeping in mind the thermodynamic and the kinetic aspects of emulsion polymerization as well as the particle size distribution [11]. This ability to control particle morphology has enhanced significantly the range of physical properties of these materials and their application in water borne coatings.

Earlier the emulsions were created by using emulsifiers and the emulsions were stabilized by the polymer capped with hydrophilic groups produced by using ionizable initiators such as persulfates [12,13] or by ionic polymers obtained by adding comonomers with ionic groups such as carboxylate monomers. There have also been reports [14,15] on various mechanisms on particle formation and growth in emulsion polymerization without emulsifier. But reports on in situ developed complex catalyzed emulsifier-free emulsion polymerization are limited to our previous publications, Cu(II)/H_2Salen/$KHSO_5$/AN/H_2O [16] and Cu(II)/glycine/$KHSO_5$/AN/H_2O [17] systems.

The present paper depicts the synthesis of PMMA by a non-conventionally initiated system involving the development of a novel, low cost, effective catalyst Cu(II)/EDTA complex, which catalyses in decomposing the initiator, ammonium persulfate (APS). The complex

* Corresponding author. Tel.: +91-674-433-360; fax: +91-674-581-850.
E-mail address: psahoochemuu@satyam.net.in (P.K. Sahoo).

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system is also found to stabilize the emulsion latex leading to a high conversion in the absence of any added emulsifier. In addition to this, detailed kinetics and size of the particles are discussed through the development of nanoparticles by the use of complex system without any added emulsifier. This is an advantage over the developed PMMA nanocomposites by conventional emulsion method with the use of emulsifier and silicates [18].

The other advantages of the non-conventional method over the conventional one are the use of a simple, low cost, novel complex initiating system instead of the choice of an emulsifier or surfactant and further to avoid the difficulty in removing the added emulsifier after the polymerization reaction [19].

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), BDH, UK was purified as reported earlier [20]. The initiator APS and all other reagents were of BDH (AR) grade and were used after purification by standard techniques.

2.2. Synthesis of PMMA

The polymerization experiments were carried out in a round-bottomed flask containing known concentrations of $CuSO_4$, EDTA and the monomer (MMA), in N_2 atmosphere. The solutions were stirred at 400–500 rpm, which helped in the formation of micelles in the complex medium. The speed in this range has no remarkable effect on the rate of polymerization. The requisite amount of the initiator solution was carefully injected to the reaction mixture. The pH of the medium at the beginning of the polymerization reaction was found to be 1.25 and at the end it was found to increase to 2.01. The reaction was stopped by keeping the flask in ice-cold water and by addition of a known excess of hydroquinone, which spontaneously consumed the unreacted free radicals. The precipitated polymers were filtered and purified by washing repeatedly with distilled water and absolute alcohol. Then they were dried till a constant weight at about 60 °C. The percentage conversion and the rate of polymerization (R_p) were determined gravimetrically.

2.3. Characterization

The visible spectra of Cu(II)/EDTA complex vis-à-vis those of the monomer and the initiator were studied using a Perkin Elmer UV–Visible spectrophotometer model Lambda-20. The particle size and morphology of PMMA samples were measured by Jeol Ltd., Japan, model number 5200 scanning electron microscope (SEM).

The average molecular weights of the purified samples were determined by widely used methods such as GPC ($\overline{M}_n$) and intrinsic viscosity ($\overline{M}_v$) using the relationship of Mark–Houwink–Sakurada [21] in pure benzene at 31 °C: $[\eta] = 5.20 \times 10^{-5} M_v^{0.7}$. Sound velocity of the sample solutions was measured with an ultrasonic interferometer, Mittal enterprises, New Delhi, India.

3. Results and discussion

In the beginning, studies on the effect of various transition metal salts coupled with EDTA on the rate of polymerization of MMA taking APS as initiator were made and the observations were recorded in Table 1. From the comparative data, Cu(II)-EDTA complex was chosen for detailed catalytic and kinetic study of polymerization.

The results of the study on the polymerization of MMA initiated by APS catalyzed by various Cu(II) salts, Cu(II)/EDTA were tabulated in Table 2. From the results it is evident that $Cu(II)SO_4$ in conjunction with EDTA gave the maximum rate of polymerization and the order of R_p for various systems is as follows:

$$R_p(\mathrm{APS} + \mathrm{CuSO_4} + \mathrm{EDTA}) > R_p(\mathrm{APS} + \mathrm{CuSO_4}) > R_p(\mathrm{APS} + \mathrm{EDTA}) > R_p(\mathrm{APS}).$$

The possibility of Cu(II)-EDTA couple initiated polymerization was excluded by the fact that no polymer was precipitated in absence of APS even after 48 h.

The UV–visible spectra of various mixtures like $Cu(II)SO_4$, Cu(II)/EDTA, Cu(II)/APS, Cu(II)/MMA, Cu(II)/EDTA/MMA, Cu(II)/EDTA/MMA/APS were measured in an aqueous solution to obtain a complete picture of the interaction between the reacting species and their relationship with the rate data (Fig. 1). The tetradentate ligand character of EDTA in alkaline medium and the same in an acidic medium with colored cations like Cu(II) to form chelate complex is well recognized [22], where the Cu(II)-EDTA ratio in complex-I (Fig. 1b and Scheme 1a) is 1:2 as evidenced by the proportionality found in the rate expression. Further, the central metal ion, Cu(II), is coordinated to two molecules of monomer, MMA (Complex-II, Scheme 1b) as revealed from the sharp change in absorbance from 0.2 (b) to 0.49 (e) in Fig. 1 which is also accorded from the rate expression. On addition of the initiator, APS, to the above mixture (Complex-II), the absorbance reduces from 0.49 (e) to 0.42 (f) showing the initiation of polymerization, thus establishing the mechanism of complex initiation. In addition, the complex formation and initiation of polymerization are also evidenced from the change in $CuSO_4$ blue color to deep blue with EDTA

Table 1
Rate of MMA polymerization (R_p) catalyzed by various transition metal salts and their couple with EDTA initiated by APS at 50 °C for 3 h

Transition metal salts	$R_p \times 10^5$ mol dm^{-3} s^{-1}	
	$[M^{2+}] = 10.0 \times 10^{-3}$ mol dm^{-3}, [EDTA] = nil	$[M^{2+}] = 10.0 \times 10^{-3}$ mol dm^{-3}, [EDTA] = 10.0×10^{-3} mol dm^{-3}
$ZnSO_4$	1.42	3.22
$CuSO_4$	2.75	3.88
$NiSO_4$	Negligible	3.44
$CoSO_4$	Negligible	Negligible
$MnSO_4$	1.25	2.04

[APS] = 10×10^{-3} mol dm^{-3}, [MMA] = 0.94 mol dm^{-3}.

Table 2
Rate of MMA polymerization (R_p) catalyzed by various Cu(II) salts, EDTA, Cu(II)/EDTA initiated by APS at 50 °C for 3 h

Chelate ligand	$R_p \times 10^5$ mol dm^{-3} s^{-1}				
	$CuSO_4$	$Cu(NO_3)_2$	$CuCl_2$	$Cu(OAc)_2$	No Cu(II) salts
No ligand	2.75	2.13	2.38	2.46	1.05
EDTA	3.88	3.11	3.23	3.31	2.01

[Cu(II)] = 10×10^{-3} mol dm^{-3}, [EDTA] = 10.0×10^{-3} mol dm^{-3}, [APS] = 10×10^{-3} mol dm^{-3}, [MMA] = 0.94 mol dm^{-3}.

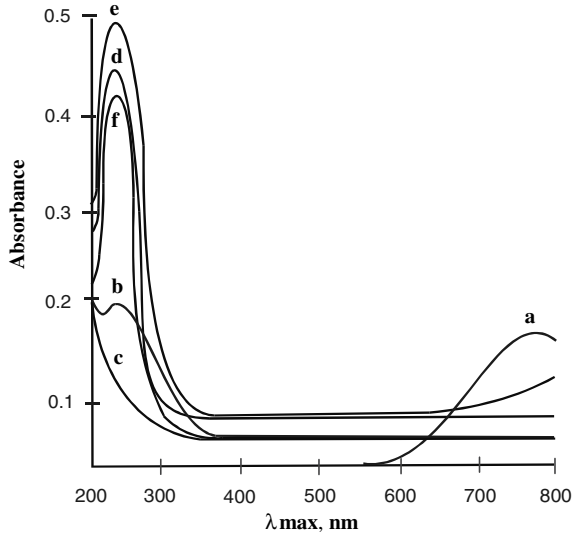


Fig. 1. Spectral evidence for the interaction of Cu(II) with EDTA, APS and MMA at [$CuSO_4$] = 10×10^{-3} mol dm^{-3}, [EDTA] = 10×10^{-3} mol dm^{-3}, [MMA] = 0.94 mol dm^{-3}, [APS] = 10×10^{-3} mol dm^{-3}: (a) $CuSO_4$, (b) EDTA + $CuSO_4$, (c) $CuSO_4$ + APS, (d) $CuSO_4$ + MMA, (e) $CuSO_4$ + EDTA + MMA, (f) $CuSO_4$ + EDTA + MMA + APS.

and the gradual fading of the blue color with reaction time by the addition of monomer and initiator. The high conversion values with Cu(II)-EDTA complex may be due to the high rate production of initiating radicals generated by the homolysis of the initiator bound by a complex of Cu(II)-EDTA where the internal energy is transferred to the initiator. The new non-conventional complex initiated system leads to stabilizing the emulsion latex to a high conversion in absence of an added emulsifier.

It was found that the conversion and the R_p were strongly affected by the monomer, initiator and complex concentration and also by the reaction time and temperature. The detailed kinetics is discussed as follows.

3.1. Variation of time

Fig. 2 shows the variation of conversion with reaction time in the temperature ranges, 35–70 °C, keeping the concentrations of MMA, APS and Cu-EDTA constant at 0.94, 10.0×10^{-3} and 10.0×10^{-3} mol dm^{-3} respectively. It was found that at all the temperatures upto 3 h of reaction, polymerization showed a dead end polymerization tendency i.e., the initiation activity of the initiator is high at initial period and hence after increases at a comparatively slow rate.

3.2. Variation of monomer concentration

The conversion and the rate of polymerization reaction increase with the increase in monomer concentration (0.470–2.353 mol dm^{-3}) at a fixed concentration of the other reagents at 50 °C. The results are tabulated in

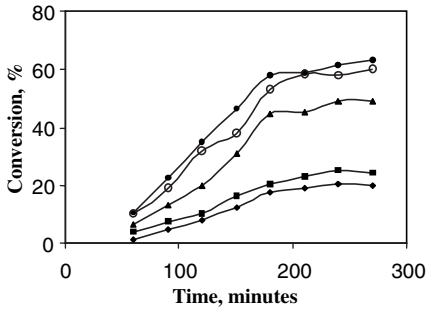


Fig. 2. Variation of % conversion with reaction time for Cu(II)-EDTA complex catalyzed polymerization of MMA with $[CuSO_4] = 10 \times 10^{-3}$ mol dm^{-3}, $[EDTA] = 10 \times 10^{-3}$ mol dm^{-3}, $[MMA] = 0.94$ mol dm^{-3}, $[APS] = 10 \times 10^{-3}$ mol dm^{-3} at various temperatures: (◆) 35 °C, (■) 40 °C, (▲) 50 °C, (●) 60 °C, (○) 70 °C.

Table 3. From the double logarithmic plot of R_p vs. [MMA], the rate of polymerization was found to be 0.75 powers dependent on the monomer concentration. This order may be attributed to the greater rate of participation of the monomer in the initiation step. Less than one value of order has also been cited in the literature as Chapiro [23] 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 or more than unity is normally observed as the polymerization system becomes heterogeneous in nature [24].

The molecular weights $\overline{M}_v$ and $\overline{M}_n$ of the polymer, as determined by viscosity and GPC methods, increase from 0.9×10^5 to 2.4×10^5 and 1.0×10^5 to 2.9×10^5 respectively with increasing [MMA] from 0.470 to 2.353 mol dm^{-3}.

3.3. Variation of initiator concentration

The effects of the R_p and the conversion have been studied by varying the concentration of the initiator in the range 5.0×10^{-3} to 25.0×10^{-3} mol dm^{-3} as given in Table 3. With the increase in APS concentration in the above range the conversion and R_p were found to increase due to an increase in concentration of the active species resulting in smaller oligomers with higher critical micelle concentration. The double logarithmic plot gave a regular increasing trend with the order of 0.57.

3.4. Variation of Cu(II)SO_4 and EDTA Concentrations

The rate of polymerization and conversion for the increase in $CuSO_4$ concentration were found to increase uniformly (Table 3). From the double logarithmic plot the order of the reaction with respect to the [Cu(II)SO_4] was found to be 0.35.

Similarly, the conversion and the rate for the increase in EDTA concentration increase to a concentration of 15.0×10^{-3} mol dm^{-3} and then they decrease slowly. This reveals that at low concentration of EDTA, the

Table 3
Effect of concentration of APS, MMA, EDTA and $CuSO_4$ on the % conversion

[MMA] mol dm^{-3}	[APS] $\times 10^3$ mol dm^{-3}	[$CuSO_4$] $\times 10^3$ mol dm^{-3}	[EDTA] $\times 10^3$ mol dm^{-3}	Nitrogen atmosphere		
				Conversion (%)	$R_p \times 10^5$ mol dm^{-3} s^{-1}	Molecular weight $\times 10^{-5}$
0.47	10.0	10.0	10.0	65.4	2.85	0.90
0.94	10.0	10.0	10.0	44.5	3.88	1.35
1.41	10.0	10.0	10.0	36.3	4.74	1.05
1.88	10.0	10.0	10.0	53.3	5.88	2.10
2.35	10.0	10.0	10.0	45.1	7.75	2.40
0.94	5.0	10.0	10.0	44.1	3.02	–
0.94	15.0	10.0	10.0	61.9	4.92	–
0.94	20.0	10.0	10.0	58.8	5.13	–
0.94	25.0	10.0	10.0	58.2	6.46	–
0.94	10.0	5.0	10.0	26.7	2.33	–
0.94	10.0	15.0	10.0	26.1	3.54	–
0.94	10.0	20.0	10.0	45.0	3.92	–
0.94	10.0	25.0	10.0	54.0	4.70	–
0.94	10.0	10.0	5.0	61.9	2.63	–
0.94	10.0	10.0	15.0	69.8	5.13	–
0.94	10.0	10.0	20.0	36.2	5.01	–
0.94	10.0	10.0	25.0	47.7	4.15	–

The polymerization rate (R_p) and molecular weight ($\overline{M}_v$) of PMMA at 50 °C for 3 h.

complex, due to the chelation of EDTA to Cu(II), helped in catalyzing the polymerization reaction but after that the tetradentate complexing ability decreases. The order of the reaction with respect to [EDTA] was found to be 0.69.

3.5. Variation of organic solvent

The polymerization reaction of MMA in presence of Cu(II)-EDTA and APS as initiator was carried out in various solvents like methanol, acetic acid and DMSO. It was found that the conversion in methanol medium was higher as compared to water medium but in all other solvents the yield was extremely low. The results were shown in Fig. 3 and it was found that [DMSO] has no effect on the rate of polymerization.

3.6. Effect of temperature and activation energy

The Arrhenius plot of log R_p vs. $1/T$ was found to be linear (Fig. 4) with a negative slope and the activation energy was computed to be 34.5 kJ/mol, which is very low as compared to the standard value 47 kJ/mol.

In most of the conventional polymerization the overall activation energy (E_a) of the polymerization is related to the activation energies of initiator decomposition (E_d), propagation (E_p) and termination (E_t) by the following equation:

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

Taking $E_p = 29$ kJ/mol, $E_t = 16$ kJ/mol reported for MMA [25] and $E_a = 34.5$ kJ/mol from Fig. 4, the activation energy for initiator decomposition was found to be E_d, 26.9 kJ/mol which is much lower than the standard value of 56.6 and 137 kJ/mol for *t*-butyl perbenzoate [26].

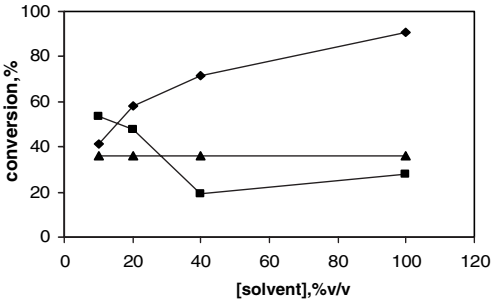


Fig. 3. Variation of % conversion with different solvent concentration at 50 °C for 3 h at $[CuSO_4] = 10 \times 10^{-3}$ mol dm^{-3}, $[EDTA] = 10 \times 10^{-3}$ mol dm^{-3}, $[MMA] = 0.94$ mol dm^{-3}, $[APS] = 10 \times 10^{-3}$ mol dm^{-3}: (◆) Methanol, (■) Acetic acid, (▲) DMSO.

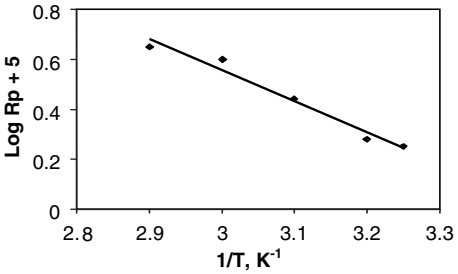


Fig. 4. Arrhenius plot of log R_p vs. $1/T$ at $[CuSO_4] = 10 \times 10^{-3}$ mol dm^{-3}, $[EDTA] = 10 \times 10^{-3}$ mol dm^{-3}, $[MMA] = 0.94$ mol dm^{-3}, $[APS] = 10 \times 10^{-3}$ mol dm^{-3}.

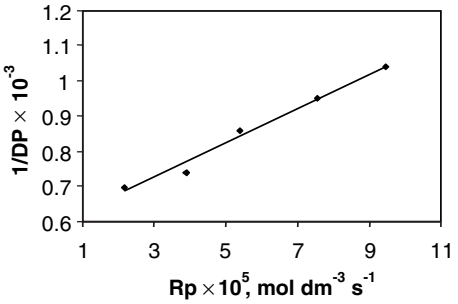


Fig. 5. Dependence of the reciprocal of degree of polymerization (1/DP) of MMA on R_p on varying [APS] from 5×10^{-3} mol dm^{-3} to 10×10^{-3} mol dm^{-3} at $[MMA] = 0.94$ mol dm^{-3}, $[CuSO_4] = 10 \times 10^{-3}$ mol dm^{-3}, $[EDTA] = 10 \times 10^{-3}$ mol dm^{-3} at 50 °C.

3.7. Chain transfer

Fig. 5 shows the relationship between R_p and the reciprocal of degree of polymerization (1/DP) of PMMA observed when the [APS] was varied at a fixed [MMA] at 50 °C. A linear relationship observed here excludes any significant chain transfer to the initiator in the polymerization of MMA with APS and Cu-EDTA complex.

3.8. Characterization

The characterization of PMMA emulsion latex was done by SEM (size and morphology), ultrasonic velocity and molecular weight measurements. For the Cu-EDTA/MMA/APS/H_2O system, the SEM data reveal that the particle size of the PMMA emulsion latex is less than 100 nm (Fig. 6a and b). Therefore, complex catalyzed emulsifier-free emulsion polymerization can

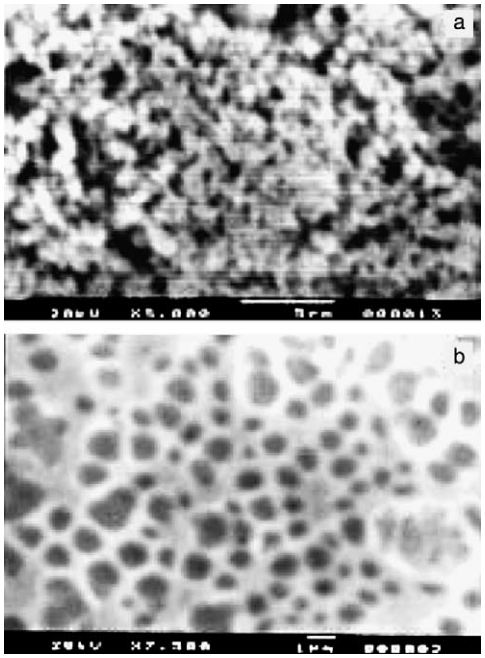


Fig. 6. (a,b) SEM micrographs of PMMA particles at different magnifications obtained by complex catalyzed emulsion polymerization at $[CuSO_4] = 10 \times 10^{-3}$ mol dm^{-3}, [EDTA] $= 10 \times 10^{-3}$ mol dm^{-3}, [MMA] $= 0.94$ mol dm^{-3}, [APS] $= 10 \times 10^{-3}$ mol dm^{-3} at 50 °C for 3 h.

hopefully be utilized to prepare nanoscale latex particles. Further the micelle number is calculated to be 5.7×10^{17} against the theoretical values of 10^{18} [19]. Ultrasonic velocity data reveal that the sound velocity increases with the increase in molecular weight (Fig. 7). The data are in good agreement with the sound velocity data of PMMA already reported [27] and similar trend was noticed in case of poly(ethylene glycol) as reported by Gerecze [28].

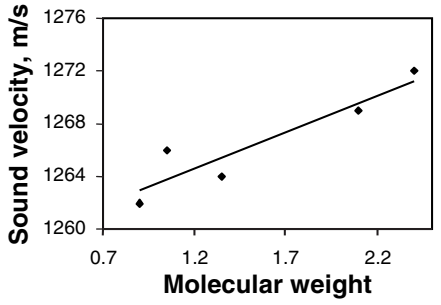


Fig. 7. Variation of sound velocity with molecular weight of PMMA solution in benzene at 30 °C.

4. Mechanism

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

1. Chain initiation by Cu(II)/EDTA complex

$$\mathrm{Cu(II)} + 2\mathrm{EDTA} \overset{\beta_1}{\rightleftharpoons} \text{Cu-EDTA Complex-I (Scheme 1a)}$$

$$\text{Complex-I} + 2\mathrm{MMA} \overset{\beta_2}{\underset{k_i}{\rightleftharpoons}} \text{Complex-II (Scheme 1b)}$$

$$\text{Complex-II} + \mathrm{S_2O_8^{-2}} \rightleftharpoons \mathrm{RM_1^{\cdot}} (\mathrm{R^{\cdot}} = \mathrm{SO_4^{-\cdot}}, \mathrm{M_1} = \mathrm{MMA})$$

The above complexation mechanism is explained earlier on the basis of the spectral data and Scheme 1a and b.

2. Propagation

$$\mathrm{RM_1^{\cdot}} + \mathrm{M} \overset{k_p}{\rightarrow} \mathrm{RM_2^{\cdot}}$$
$$\vdots \qquad\qquad \vdots$$
$$\mathrm{RM_{n-1}^{\cdot}} + \mathrm{M} \overset{k_p}{\rightarrow} \mathrm{RM_n^{\cdot}}$$

3. Termination

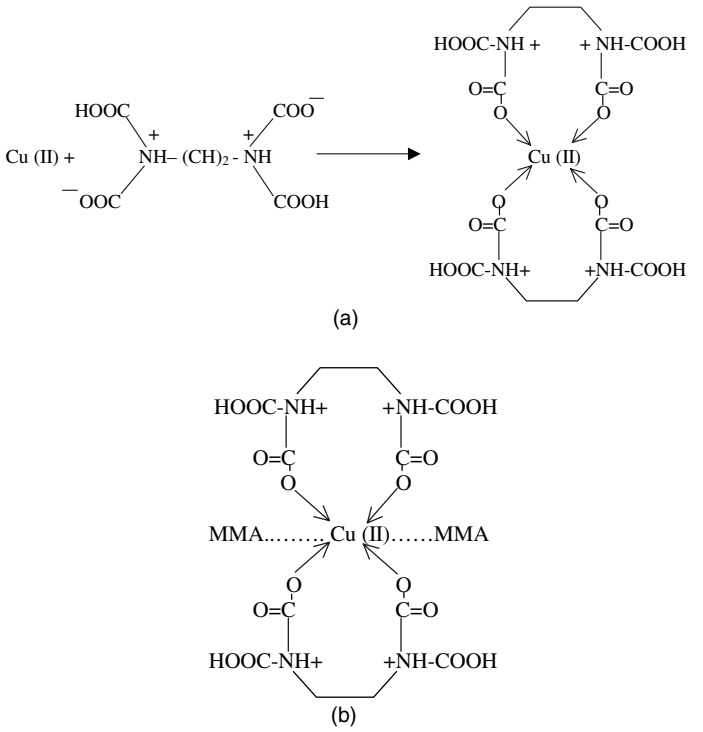
$$\mathrm{RM_n^{\cdot}} + \mathrm{RM_m^{\cdot}} \overset{k_{t1}}{\rightarrow} \text{Polymer}$$

$$\mathrm{RM_n^{\cdot}} + \text{Cu(II)-Complex} \overset{k_{t2}}{\rightarrow} \text{Polymer} + \text{Cu(I)-Complex} + \mathrm{H^+}$$

Applying steady state principles and assuming mutual termination, the rate expression is observed as follows: $R_p \propto [\mathrm{Cu(II)}]^{0.35}[\mathrm{EDTA}]^{0.69}[\mathrm{APS}]^{0.57}[\mathrm{MMA}]^{0.75}$.

5. Conclusion

Complex catalyzed emulsion polymerization of MMA has been significantly carried out and factors affecting the polymerization have been investigated. Surfactant is not necessary for the system as the complex most likely plays the role of a surfactant/emulsifier in stabilizing the emulsion latex. The polymer latexes were characterized by SEM (size and morphology), ultrasonic velocity and molecular weight measurements. Nanoscale latex particles could be obtained without emulsifier than in a conventional emulsion polymerization. Hence, it is a promising technique for the preparation of polymer



Scheme 1. (a) Formation of Cu(II)-EDTA complex (Complex-I), (b) coordination of monomer, MMA with Cu(II)-EDTA (Complex-II).

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

Acknowledgement

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