Polymerization of methyl methacrylate in the presence of molecular oxygen — a kinetic study

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Methyl methacrylate was polymerized in aqueous medium initiated by a copper(II)-ascorbic acid-oxygen system at 40°C and a kinetic study of the reaction is presented. The rate of polymerization, R_p showed an increase, constancy and then a decrease with increase in the $[Cu^{2+}]$. The order with respect to $[Cu^{2+}]$ was 0.5 in the rate increase region. The order in monomer concentration changed gradually from 1.0 to 2.0 with increase in $[Cu^{2+}]$. R_p became independent of ascorbic acid (AA) concentration and oxygen concentration at high concentrations. These results indicate that termination by mutual interaction of chain radicals predominates at low $[Cu^{2+}]$ while termination was exclusively by metal ions at high $[Cu^{2+}]$. R_p was also observed to increase with temperature and ionic strength and to $K_p/K_t^{1/2}$ value was calculated and compared with literature values. Chain lengths were determined by viscometry for the polymers obtained under various experimental conditions.

INTRODUCTION

The initiation of vinyl polymerization in aqueous medium by redox catalysts has been the subject of extensive investigations. In free radical polymerizations, oxygen acts as an inhibitor resulting in large induction periods[1,2]. Little attention was shown to those systems containing oxygen as one of the components of the initiating system wherein oxygen facilitates primary radical production and thereby increasing the rate of polymerization. Oxygen may react with the reducing agent, producing additional radicals over those produced from the usual redox reaction between oxidant and reductant[3] or, oxygen may reoxidize the reduced oxidant resulting in the production of radicals in addition to the radicals produced from the redox reaction[4-7]. In addition oxygen can form a monomeric peroxide to set up a redox pair with reducing agent[8] or oxygen can directly enter into the redox reaction with some reducing agents[9,10]. In addition to this, oxygen can initiate the polymerization of methyl methacrylate itself above 100°C[11]. We present here the results on the aqueous polymerization of methyl methacrylate initiated by the copper(II)-ascorbic acid-oxygen system.

EXPERIMENTAL

Materials

Methyl methacrylate (Rohm and Haas) was freed from inhibitor with alkali, washed, dried over anhydrous sodium sulphate, distilled under reduced pressure and stored at 5°C. Ascorbic acid (G.R., Sarabhai M. Chemicals) and copper sulphate (A.R., B.D.H.) were used without further purification. Freshly prepared ascorbic acid solutions were always used to prevent aerial oxidation. High purity oxygen gas was supplied by Indian Oxygen Ltd. Water distilled (× 3) in an all glass quick-fit set-up was used for the preparation of the solutions. Potassium nitrate and sulphuric acid (A.R., B.D.H.) were used as such. Double distilled benzene (A.R., B.D.H.) was used as the solvent for the viscosity measurements.

Methods

The polymerization was conducted at 40° ±0.1°C in pyrex glass tubes with gas inlet and outlet arrangements. Copper(II) solution was placed in the thermostatically controlled reaction tube and oxygen was passed at the rate of 50 cc per min into the reaction solution for 25 min till the solution was saturated with oxygen as determined by Winkler's method[12] (*Table 1*). The monomer was then added followed by ascorbic acid. Polymerization started within a few minutes as indicated by the appearance of turbidity. Cooling in a freezing mixture was adopted to arrest the polymerization. The polymer formed was filtered off and dried at 50°C overnight. The rate of polymerization, R_p was evaluated from the weight of the polymer.

The oxygen concentration was varied by passing mixtures of different compositions of oxygen and nitrogen. The oxygen content in the solution was observed to increase linearly with the composition of oxygen in the gas mixture up to its saturation value (8.3×10^{-4} M at 40°C).

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Table 1 Oxygen concentration in the reaction system with oxygen flow time

Time of O_2 flow (min)	5	10	15	20	25	30	40	50
$O_2 \times 10^4$ M	5.20	6.55	7.28	8.25	8.31	8.42	8.41	8.37

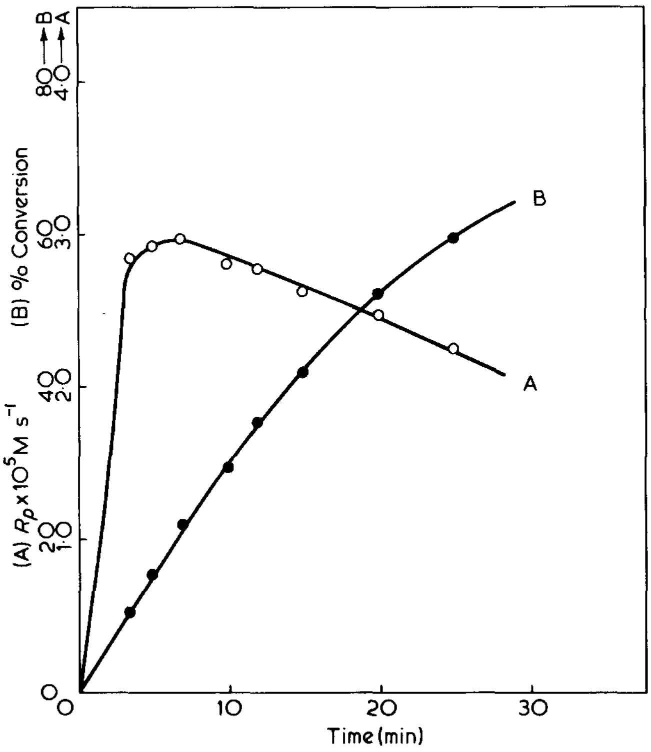

Figure 1 Attainment of steady state: (A), R_p vs. time; (B), % monomer conversion vs. time; $[Cu^{2+}] = 2 \times 10^{-5}$ M; [AA] = 2×10^{-3} M; $[O_2] = 8.3 \times 10^{-4}$ M; [MMA] = 5.63×10^{-2} M; Temperature = 40°C

Chain length 'n' of the purified polymethyl methacrylate was determined viscometrically using an Ubbelohde suspended level dilution viscometer kept in a viscometric bath whose temperature was maintained to ±0.01°C. The Mark–Houwink relation employed was:

$$n = 2.81 \times 10^3\ [\eta]^{1.32} \text{ in benzene at } 25°C^{13}$$

RESULTS AND DISCUSSION

Ascorbic acid and oxygen did not initiate polymerization under our experimental conditions. There was polymerization without an induction period at high $[Cu^{2+}]$ but the rate was observed to be low. With low $[Cu^{2+}]$, higher rates were obtained but only with a considerable induction period (10–20 min). The appearance of the turbidity was taken as the zero time for rate measurements. The steady state rate was obtained within 10 min, below 30% conversion (*Figure 1*).

Effect of copper(II) concentration

The effect of $[Cu^{2+}]$ ($0.8 - 20 \times 10^{-5}$ M) was studied at constant [MMA], [AA] and $[O_2]$. R_p increased with $[Cu^{2+}]$ up to $\sim 2 \times 10^{-5}$ M with an order 0.5 (*Figure 2*) remained almost constant for $[Cu^{2+}]$ $\sim 2 \times 10^{-5}$ M to 6×10^{-5} M and decreased at higher $[Cu^{2+}]$ (*Table 2*).

Similar observations on the dependence of R_p on $[Cu^{2+}]$ were reported both when it was used as an oxidant[14] and as a catalyst[15]. Parallel results were observed for the influence of ferric[16,17] and ceric concentrations[18] on the kinetics of vinyl polymerization. This was explained on the basis of metal ion participation in the production of the primary radicals at low concentrations of the metal ion causing an increase in rate and the participation of the metal ion in the termination process at higher concentrations resulting in a rate decrease. Saccubai and Santappa[19] who observed a similar trend in R_p with vanadium (V) concentration considered that the rate decrease was due to the oxidation of the primary radicals by the metal ion. In the present study the rate decrease with $[Cu^{2+}] > 6 \times 10^{-5}$ M may be due to the oxidation of the primary radicals by Cu^{2+} or to the participation of the metal ion in the termination process or both.

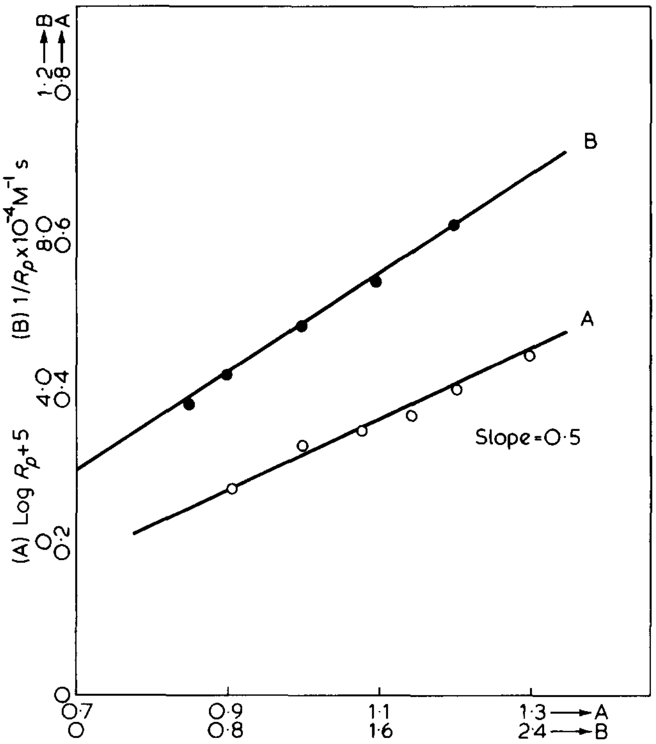

Figure 2 Dependence of R_p on $[Cu^{2+}]$: (A), log R_p vs. log$[Cu^{2+}]$ (at low $[Cu^{2+}]$ values); (B), $1/R_p$ vs. $[Cu^{2+}]$ (at high $[Cu^{2+}]$ values); [AA] = 2×10^{-3} M; $[O_2] = 8.3 \times 10^{-4}$ M; [MMA] = 5.63×10^{-2} M; Temperature = 40°C

Table 2 Dependence of R_p and n on $[Cu^{2+}]$; [AA] = 2.0×10^{-3} M; $[O_2] = 8.3 \times 10^{-4}$ M; [MMA] = 5.63×10^{-2} M; temperature = 40°C

$[Cu^{2+}] \times 10^5$ M	$R_p \times 10^5$ M s^{-1}	n
0.8	1.85	443
1.2	2.21	416
1.6	2.50	398
2.0	2.79	361
3.0	2.88	370
4.0	2.82	328
5.0	2.80	344
6.0	2.85	316
8.0	2.28	289
12.0	1.75	292
16.0	1.48	250
20.0	1.20	214

Table 3 Dependence of R_p and n on $[O_2]$ at high $[O_2]$; $[Cu^{2+}] = 3.0 \times 10^{-5}$ M; [AA] $= 2.0 \times 10^{-3}$ M; [MMA] $= 5.63 \times 10^{-2}$ M; temperature = 40°C

Time of O_2 flow (min)	$[O_2] \times 10^4$ M	$R_p \times 10^5$ M s^{-1}	n
5	5.20	2.67	315
10	6.55	2.79	–
15	7.28	2.80	301
20	8.25	2.79	298
25	8.31	2.83	312
30	8.42	2.75	336
40	8.41	2.81	303

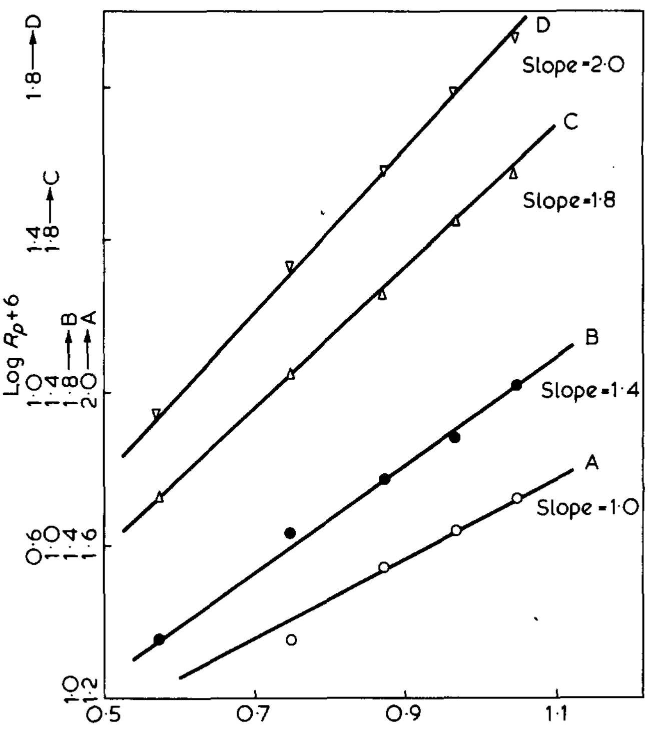

Figure 3 Plots of log R_p vs. log [MMA] at different $[Cu^{2+}]$; [AA] $= 2 \times 10^{-3}$ M; $[O_2] = 8.3 \times 10^{-4}$ M; Temperature = 40°C; (A), $[Cu^{2+}] = 1.2 \times 10^{-5}$ M; (B), $[Cu^{2+}] = 1.6 \times 10^{-5}$ M; (C), $[Cu^{2+}] = 3.0 \times 10^{-5}$ M; (D), $[Cu^{2+}] = 1.0 \times 10^{-4}$ M

Effect of monomer concentration

[MMA] was varied from 3.75×10^{-2} M to 11.3×10^{-2} M at different $[Cu^{2+}]$ values. R_p increased with increase in [MMA] and log R_p vs. log [MMA] plot gave slopes varying from 1 to 2 with increase in $[Cu^{2+}]$ (*Figure 3*). The orders with respect to [MMA] were 1.0, 1.8 and 2.0 in the $[Cu^{2+}]$ regions where R_p increased, was independent and decreased with $[Cu^{2+}]$ respectively. Similar observations were made in the Ce^{4+}-cyclohexanone[18] and Ce^{4+}-glycerol initiating systems[20] wherein the order with respect to [monomer] changed from 1.5 to 2.0 with increase in the metal ion concentration. This change in the order was attributed to the transition in the termination mechanism from a mutual to a linear type. The observed dependence of R_p on [MMA] in the present study may also be due to the change in the mode of termination mechanisms.

Effect of oxygen concentration

Polymerization occurred even in the absence of oxygen due to the production of initiating radicals from the AA–Cu^{2+} reaction[21], but the rate was low (0.47×10^{-5} M s^{-1}) as compared to that in the presence of oxygen (2.8×10^{-5} M s^{-1}). R_p increased with $[O_2]$ up to 6.5×10^{-4} M and thereafter remained constant (*Table 3*). The order with respect to $[O_2]$ was 0.5 at low $[Cu^{2+}]$ (*Figure 4*). At high $[Cu^{2+}]$ the order was higher (0.7). The extent of monomer conversion at chosen intervals of time for different compositions of oxygen was also studied (*Figure 5*).

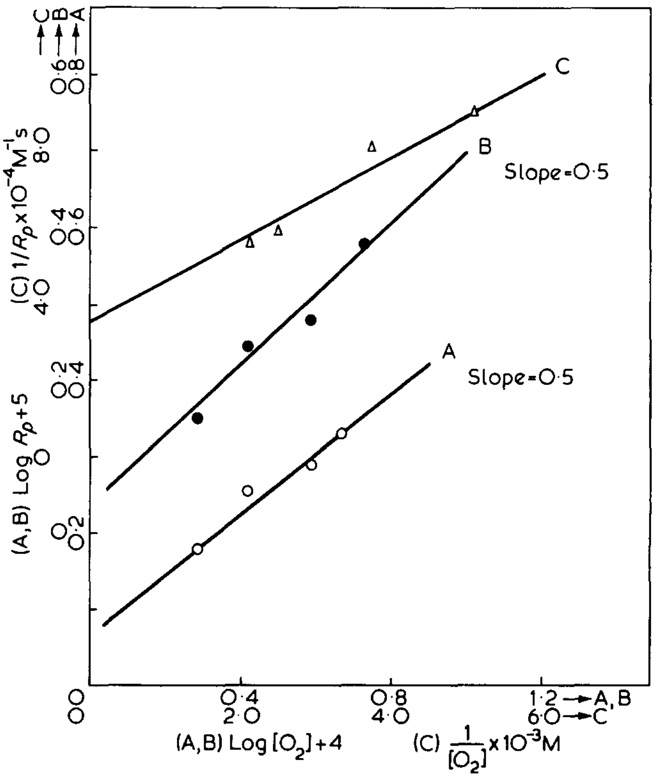

Figure 4 Dependence of R_p on $[O_2]$ at different $[Cu^{2+}]$; (A,B), log R_p vs. log $[O_2]$; (C), $1/R_p$ vs. $1/[O_2]$; [AA] $= 2 \times 10^{-3}$ M; [MMA] $= 5.63 \times 10^{-2}$ M; Temperature = 40°C; (A), $[Cu^{2+}] = 2 \times 10^{-5}$ M; (B), $[Cu^{2+}] = 5 \times 10^{-5}$ M; (C), $[Cu^{2+}] = 1 \times 10^{-4}$ M

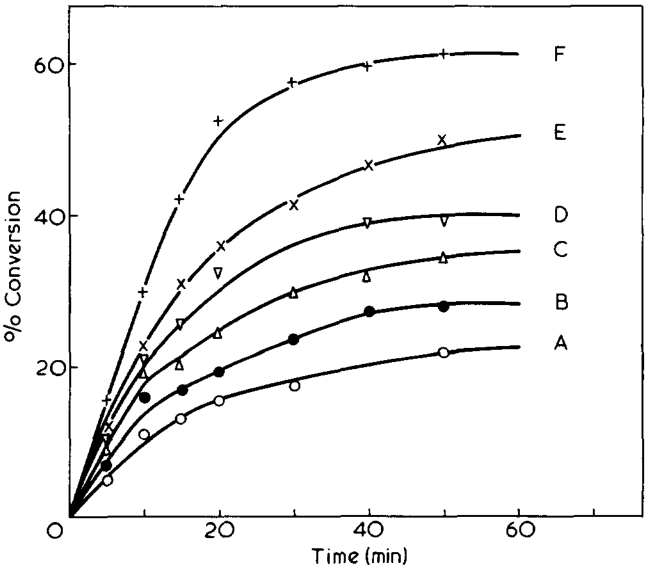

Figure 5 Percentage monomer conversion vs. time at different O_2 compositions: $[Cu^{2+}] = 2 \times 10^{-5}$ M; [AA] $= 2 \times 10^{-3}$ M; [MMA] $= 5.63 \times 10^{-2}$ M; Temperature = 40°C; A, 22%; B, 34%; C, 46%; D, 67%; E, 80%; F, 100%

Table 4 Dependence of R_p and n on [AA] at different [Cu^{2+}]; [O_2] = 8.3 x 10^{-4} M; [MMA] = 5.63 x 10^{-2} M; temperature = 40°C

	[Cu^{2+}] = 2.0 x 10^{-5} M		[Cu^{2+}] = 5.0 x 10^{-5} M		[Cu^{2+}] = 1.2 x 10^{-4} M	
[AA] x 10^3 M	R_p x 10^5 M s^{-1}	n	R_p x 10^5 M s^{-1}	n	R_p x 10^5 M s^{-1}	n
1.0	0.847	–	0.818	–	0.798	–
1.1	2.820	327	2.780	314	1.840	292
1.2	2.810	318	2.810	341	1.860	273
1.4	–	–	–	–	1.910	302
1.6	2.620	351	2.840	326	–	–
2.0	2.810	332	2.800	319	1.880	281
4.0	2.830	290	2.780	298	1.860	–
6.0	2.660	292	2.860	–	1.940	269
8.0	2.720	310	2.850	332	1.850	311

The 0.5 order dependence of R_p on [O_2] was also reported earlier when oxygen was used as a component of the initiating system[22]. The independence of R_p on [O_2] at higher concentrations of the latter may be due to a balance of the following opposing effects: (a) an increase in the production of primary radicals with increase in [O_2]; (b) scavenging of primary radicals by oxygen; and (c) termination by oxygen.

Effect of ascorbic acid concentration

Ascorbic acid concentration was varied at three different [Cu^{2+}]. R_p was found to be independent of [AA] above a particular concentration. A sudden increase in R_p with a small increase in [AA] made the determination of the order difficult. R_p remained constant at [AA] > 1.1 $\times 10^{-3}$ M and there was no polymerization below [AA] $= 0.9 \times 10^{-3}$ M (*Table 4*). The independence of R_p on [AA] in a particular concentration range was reported in the previous investigations also[3,23]. The observed independence of R_p on [AA] may be explained as follows. Since [AA] used was high compared with [O_2] and [Cu^{2+}] the complex concentration and hence the initiation rate would be unaffected by the variation in [AA].

Effect of hydrogen ion concentration

[H^+] was varied with dilute H_2SO_4 at constant ionic strength. R_p decreased with the increase in [H^+] while the induction period increased (*Table 5*). The rate of oxidation of AA by O_2 in the presence of Cu^{2+} ions was observed to decrease with increasing [H^+][24]. The added protons may decrease the rate of dissociation of AA and hence the complex concentration resulting in the decreased rate of production of initiating radicals.

Effect of ionic strength

Ionic strength of the medium was varied with KNO_3 (0.1–0.5 M) when R_p increased nearly by 50% (*Table 5*). The rate increase may be due to the increased complex concentration arising from the increased rate of dissociation of AA.

Effect of temperature

R_p increased with temperature from 31.6°C to 45°C with the decrease in induction period. The energy of activation was calculated to be 7.4 kcal mol^{-1} from the Arrhenious plot (*Figure 6*).

Table 5 Dependence of R_p and n on [H_2SO_4] and μ; [AA] = 2.0 x 10^{-3} M; [MMA] = 5.63 x 10^{-2} M; [O_2] = 8.3 x 10^{-4} M; temperature = 40°C

[Cu^{2+}] = 4.0 x 10^{-5} M; μ = 2.5 x 10^{-3} M			[Cu^{2+}] = 2.0 x 10^{-5} M	
[H_2SO_4] x 10^3 M	R_p x 10^5 M s^{-1}	n	μ M	R_p x 10^5 M s^{-1}
–	2.88	377	–	2.75
0.5	2.87	379	0.1	2.82
1.0	2.81	420	0.2	2.97
1.5	2.66	–	0.3	3.14
2.0	2.57	556	0.4	3.53
2.5	2.60	497	0.5	3.86

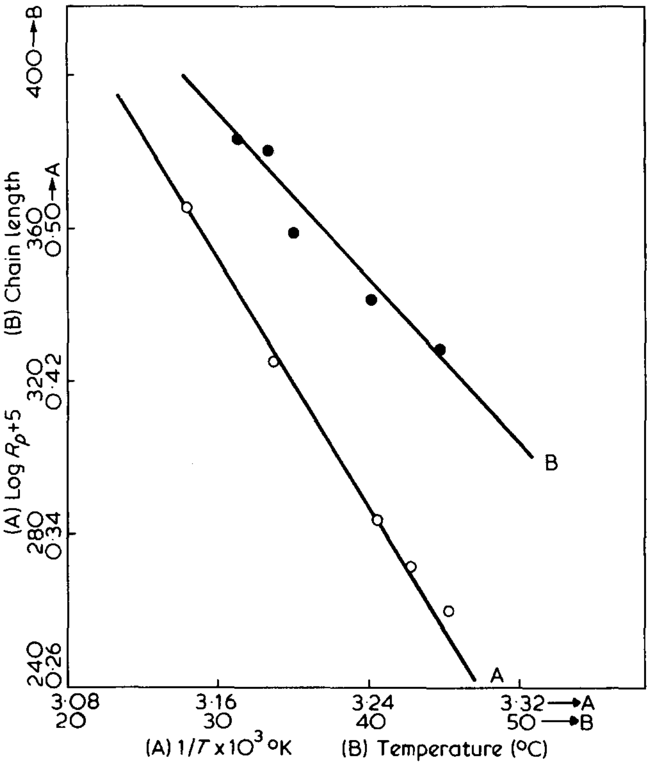

Figure 6 Dependence of R_p and n (chain length) on temperature; (A), log R_p vs. $1/T$; (B), n vs. temperature; [Cu^{2+}] = 2 x 10^{-5} M; [AA] = 2 x 10^{-3} M; [O_2] = 8.3 x 10^{-4} M; [MMA] = 5.63 x 10^{-2} M

Chain length

Chain lengths increased with [MMA] (*Figure 7*) decreased with [Cu^{2+}] (*Table 2*) and were unaffected by variation in [AA] (*Table 4*). 'n' values decreased with [O_2] at low concentrations (*Figure 8*) and remained almost constant in the concentration region where there was no

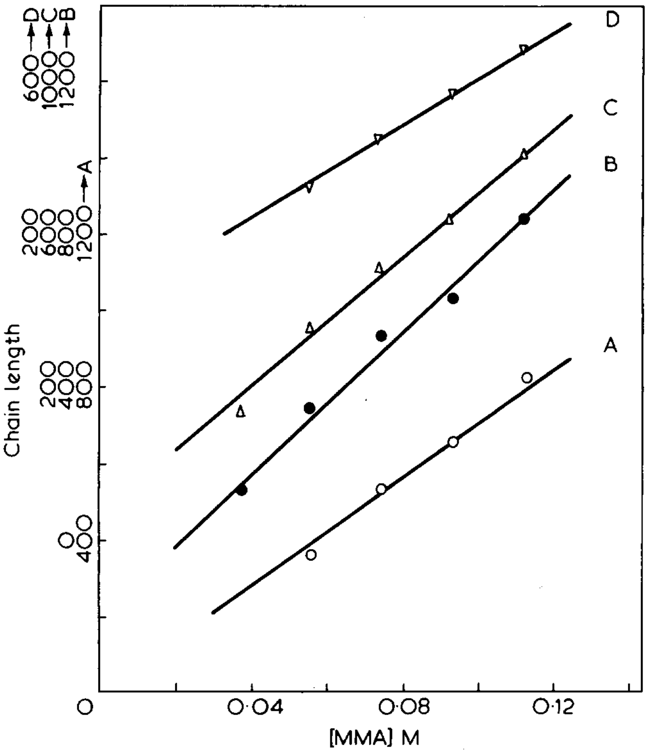

Figure 7 Plots of n (chain length) vs. [MMA] at different [Cu^{2+}]: [AA] = 2×10^{-3} M; [O_2] = 8.3×10^{-4} M; Temperature = 40°C; (A), [Cu^{2+}] = 1.2×10^{-5} M; (B), [Cu^{2+}] = 1.6×10^{-5} M; (C), [Cu^{2+}] = 3.0×10^{-5} M; (D), [Cu^{2+}] = 1.0×10^{-4} M

increase in R_p with [O_2] (*Table 3*). Similar dependence of chain lengths on $[O_2]^{4,9,25,27}$ and $[Cu^{2+}]^{28,29}$ were also reported in previous investigations. 'n' increased with [H^+] (*Table 5*) and decreased with temperature (*Figure 6*).

Reaction mechanism and rate law

The kinetic results may be explained with the following mechanism:

(1) Production of primary radicals[24]

$$AA + O_2 + Cu^{2+} \overset{K}{\rightleftharpoons} \text{complex} \xrightarrow{k_1} R\cdot \text{ etc}$$

where R· denotes the various free radicals produced.

(2) Initiation

$$R\cdot + M \xrightarrow{k_i} M\cdot$$

(3)Propagation

$$M^{\cdot}_{n-1} + M \xrightarrow{k_p} M^{\cdot}_n$$

where $n > 1$.

(4) Termination

(a) Mutual termination

$$2M^{\cdot}_n \xrightarrow{k_{t1}} \text{polymer}$$

(b) Linear termination

$$M^{\cdot}_n + Cu^{2+} \xrightarrow{k_{t2}} \text{polymer} + Cu^{+}$$

(c) Termination by oxygen

$$M^{\cdot}_n + O_2 \xrightarrow{k_{t3}} \text{products}$$

(d) Termination by primary radicals

$$M^{\cdot}_n + R \xrightarrow{k_{t4}} \text{polymer}$$

(5) Deactivation of primary radicals

$$R\cdot + Cu^{2+} \xrightarrow{k_2} \text{products}$$

$$R\cdot + O_2 \xrightarrow{k_3} \text{products}$$

The rate expression for monomer disappearance, R_p was derived assuming stationary state concentrations for free radicals and non-dependence of rate constants k_p and k_t on chain length.

Assuming initiation by R· and termination by mutual interaction the rate expression for monomer disappearance would be

$$R_p = \frac{k_p}{k_{t1}^{1/2}}[M]\left[\frac{k_1 k_i[\text{Complex}][M]}{(k_i[M] + k_2[Cu^{2+}] + k_3[O_2])}\right]^{1/2} \quad (1)$$

At high [AA], the complex concentration varies linearly with [Cu^{2+}] and [O_2] only, while remaining independent of [AA]. Now the equation becomes:

$$R_p = \frac{k_p}{k_{t1}^{1/2}}[M]\left[\frac{K k_1 k_i[O_2][Cu^{2+}][M]}{(k_i[M] + k_2[Cu^{2+}] + k_3[O_2])}\right]^{1/2} \quad (2)$$

Assuming initiation by R· and termination by metal ion, the expression for R_p would be equation 3

$$R_p \frac{k_p}{k_{t2}} \frac{K k_1 k_i[O_2][M]^2}{(k_i[M] + k_2[Cu^{2+}] + k_3[O_2])} \quad (3)$$

Low [Cu^{2+}] *where* $R_p \propto [Cu^{2+}]$

Initiation by R· and termination by mutual interaction of polymer radicals is considered. Under conditions $k_i[M] \gg k_2[Cu^{2+}] + k_3[O_2]$ equation 2 may be written as equation 4

$$R_p = \frac{k_p}{k_{t1}^{1/2}}[M](K k_1[O_2][Cu^{2+}])^{1/2} \quad (4)$$

Experimentally determined orders, i.e. first order with respect to [MMA] and 0.5 order with respect to [Cu^{2+}] and [O_2] are in agreement with the rate expression equation 4. It was observed that the order with respect to [MMA] increased with further increase in [Cu^{2+}]. The assumption k_i[M] increased with further increase in [Cu^{2+}]. The assumption $k_i[M] \gg k_2[Cu^{2+}] + k_3[O_2]$ was justifed since [Cu^{2+}] is low as compared with [MMA] and a major portion of oxygen present in the system is involved in complex formation with AA and Cu^{2+}.

Intermediate [Cu^{2+}] *where* R_p *was independent of* [Cu^{2+}]

Assuming initiation by R· and termination by mutual interaction of polymer radicals, under conditions k_i [M]

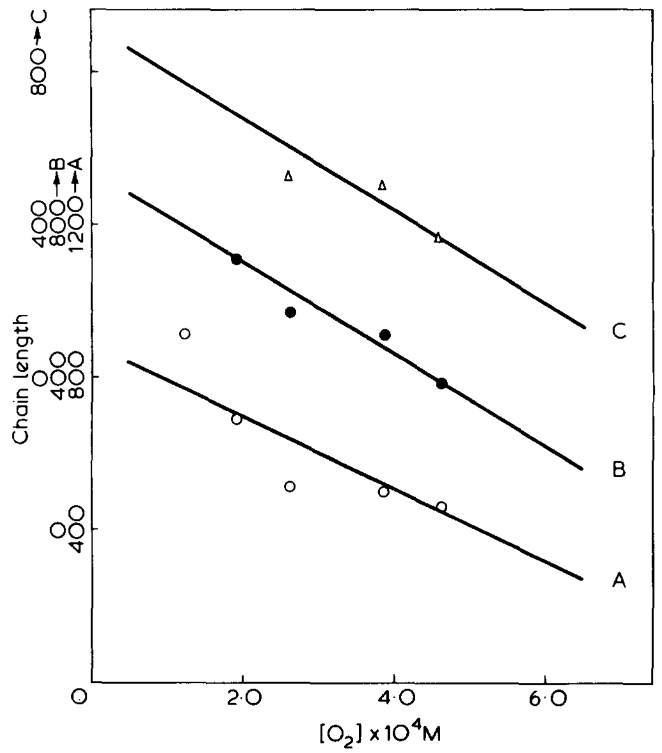

Figure 8 Plots of *n* (chain length) vs. $[O_2]$ at different $[Cu^{2+}]$: $[AA] = 2 \times 10^{-3}$ M; $[MMA] = 5.63 \times 10^{-2}$ M; Temperature = 40°C; (A), $[Cu^{2+}] = 2 \times 10^{-5}$ M; (B), $[Cu^{2+}] = 5 \times 10^{-5}$ M; (C), $[Cu^{2+}] = 1 \times 10^{-4}$ M

Table 6 $k_p/k_t^{1/2}$ value of MMA obtained in the present investigation

Plots	$k_p/k_t^{1/2}$ $(M^{-1/2}\,s^{-1/2})$
R_p vs. $[MMA]^{1.0}$	0.115
R_p vs. $[Cu^{2+}]^{0.5}$	0.112
R_p vs. $[O_2]^{0.5}$	0.116

$+k_3[O_2] \ll k_2[Cu^{2+}]$ we can get

$$R_p = \frac{k_p}{k_{t1}^{1/2}}[M]^{3/2}\left[\frac{K\,k_1\,k_i[O_2]}{k_2}\right]^{1/2} \tag{5}$$

Experimental results are in good agreement with equation 5 at intermediate $[Cu^{2+}]$. The assumption $k_i[M] + k_3[O_2] \ll k_2[Cu^{2+}]$ was quite valid at intermediate $[Cu^{2+}]$, since there will be competition between Cu^{2+} and the monomer for primary radicals and the equilibrium $[O_2]$ will also be low. Generally, the independence of R_p on metal ion concentration was explained by the metal ion oxidation of primary radicals. Ganga Devi and Mahadevan[30] in their study on the polymerization of AN and MMA initiated by the Mn^{3+}–malonic acid system observed rate dependence on $[M]^{3/2}$, [malonic acid]$^{0.5}$ and $[Mn^{3+}]^0$. These results were explained on the basis of mutual termination and the preponderance of the primary radical oxidation by Mn^{3+} over the reaction between primary radicals and monomer. Subramanian and Santappa[18] have given a similar explanation for the independence of R_p on $[Ce^{4+}]$ in the polymerization of MMA initiated by the Ce^{4+}–malonic acid system. However Elayaperumal[31] assumed linear termination to explain the rate independence on Thallium(III) concentration. Our results, however, are not in agreement with the rate expression derived assuming metal ion termination.

High $[Cu^{2+}]$ where R_p decreased with $[Cu^{2+}]$

Assuming initiation by primary radicals and linear termination by Cu^{2+}, with high [AA] we get equation 3. On rearranging, equation 3 can be written as equation 6.

$$1/R_p = \frac{k_i k_{t2}[M] + k_3 k_{t2}[O_2] + k_2 k_{t2}[Cu^{2+}]}{k_p K\,k_1\,k_i[O_2][M]^2} \tag{6}$$

Equation 6 satisfies all the experimental results at high $[Cu^{2+}]$. Further, plots of $1/R_p$ vs. $[Cu^{2+}]$ (*Figure 2*) and $1/R_p$ vs $1/[O_2]$ (*Figure 4*) gave straight lines with intercepts on *Y*-axis verifying equation 6. Similar kinetics were realized in many redox initiated polymerizations of vinyl monomers[30,32].

A decrease in rate with metal ion concentration was also reported for systems containing Ce^{4+},[20] V^{5+},[19] Mn^{3+},[30] Cr^{6+},[33] which was attributed to termination by metal ions. Such metal ion terminations by both oxidative[30,34] and reductive mechanisms[35] have been well established. Termination by Cu^{2+} was reported in the polymerization of MMA[14,36], acrylamide[37,38], acrylonitrile[39,40], acrylic acid[28] and styrene[41,42]. The mechanism of termination by Cu^{2+} was by electron transfer from a propagating polymer radical to the d-orbital of the cation[43].

Generally chain lengths increase with [MMA] (*Figure 7*) and decrease with $[O_2]$ (*Figure 8*) and $[Cu^{2+}]$ (*Table 2*) in agreement with the given mechanisms.

Rate constants $k_p/k_t^{\frac{1}{2}}$

The $K\,k_1$ value was calculated to be 3.47×10^6 M s^{-1} at 40°C from the oxidation studies[24] and using this, $k_p/k_t^{1/2}$ values were obtained from equation 4 (*Table 6*). It is surprising that $k_p/k_t^{1/2}$ values obtained in the present investigation in precipitating medium is comparable with the value reported (~0.05) in the homogeneous polymerization[44]. Baxendale *et al.*[45] using the redox initiator Fe^{2+}–H_2O_2 in aqueous medium estimated $k_p/k_t^{1/2}$ for MMA polymerization to be 12.3 at 25°C, while the value 5.2×10^{-2} was reported for the bulk polymerization. Similarly Evans, Santappa and Uri[46] obtained the value of 0.27 using Fe^{3+} Cl^- as the photosensitizer in the precipitating media. Atkinson and Cotten[47] using $Fe^{3+}OH^-$ as the initiator reported a $k_p/k_t^{1/2}$ value of 0.5581 at 25°C in aqueous medium. Santappa with Subramanian[18], Mahadevan[48], Nagabhushanam[49], Sheriff[50] and Anwaruddin[51] reported the $k_p/k_t^{1/2}$ values ranging from 0.3 to 1.43 for MMA polymerization with different initiating systems in the aqueous medium. These high values of $k_p/k_t^{1/2}$ may be explained by the general theory of heterogeneous polymerization in the precipitating media developed by Bamford and Jenkins[52], wherein they envisaged a finite possibility of shielding of the active end of the growing polymer radical resulting in a decrease in the termination constant. The radical ends will have little difficulty as far as propagation is concerned and this would result in high values of $k_p/k_t^{1/2}$.

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