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Kinetics of the Ruthenium(III) and Palladium(II) Catalysed Polymerization of Methylmethacrylate by Aminoalcohols in Presence of CCl_4

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Ruthenium(III) and palladium(II) catalysed polymerization of methylmethacrylate (MMA) with aminoalcohols, *viz.*, ethanolamine (EA) and diethanolamine (DEA) has been studied in presence of CCl_4 and in dimethylsulfoxide (DMSO) medium by employing a dilatometric technique at 60°C. The rate of polymerization (R_p) of MMA is proportional to [MMA], $[\text{Aminoalcohol}]^{1/2}$, $[CCl_4]^{1/2}$ and $\{k' + k''[\text{Catalyst}]^{1/2}\}$, where k′ and k″ are rate constants for uncatalysed and catalysed path of polymerization respectively. At higher CCl_4 concentration when $[CCl_4]/[\text{Aminoalcohols}] > 1$, the rate of polymerization becomes independent of $[CCl_4]$. The rate of polymerization is inhibited by hydroquinone, suggesting a free radical mechanism. Mechanism involving the charge-transfer complex between {Aminoalcohol-Catalyst} complex and CCl_4 has been suggested for the initiation of polymerization of Methylmethacrylate.

INTRODUCTION

Platinum group metal-ions as homogeneous catalyst have widely been used in several redox-reactions. However, not much attention has been diverted on the use of these metal-ions in polymerization reactions. The catalytic effect of $RuCl_3$ and $PdCl_2$ and their complexes on the polymerization of olefins and acetylenes has been discussed in detail[1, 2]. It has been observed that initiation of polymerization of methylmethacrylate (MMA) involves the formation of charge transfer complex between {metal-ion-amine} species and CCl_4. In order to examine the role of these catalysts in polymerization of MMA we have studied the detail kinetics of ruthenium(III) and palladium(II) catalysed polymerization of methylmethacrylate (MMA) by aminoalcohols, *viz.*, ethanolamine (EA) and diethanolamine (DEA) in presence of CCl_4 and in dimethylsulfoxide (DMSO) medium and results are reported in the present communication.

EXPERIMENTAL

MMA, DMSO and CCl_4 were purified before use. Ethanolamine and diethanolamine (AR grade) were distilled under reduced pressure. $RuCl_3$ or $PdCl_2$ (Loba, AR grade) solution was prepared by dissolving the sample in very dilute HCl (0.01 mol dm^{-3}) and was stored in black-coated bottles to avoid photochemical effects.

The polymerization of MMA was carried out in a dilatomter[3] (bulb capacity 5 mL, with a 11 cm long capillary of 3 mm diameter) under nitrogen atmosphere at 60°C using DMSO as solvent. The required amounts of aminoalcohol, MMA, $RuCl_3/PdCl_2$, CCl_4 and DMSO were taken in the dilatometer which was immediately sealed and placed in a thermostatic bath maintained at 60 ± 1°C. Progress of the reaction was monitored with the help of a cathetometer. The polymerization was not allowed to proceed beyond 20% to avoid the effects due to increase in the viscosity[4]. The polymer was precipitated with acidified methanol and dried to a constant weight.

Evaluation of Rate of Polymerization

The rate of polymerization of MMA is given as

$$R_p\ (\text{mol dm}^{-3}\ \text{s}^{-1}) = \frac{w \times 10^3}{t \times 60 \times 100.12} \qquad \text{(a)}$$

where w is the weight of polymer obtained from 1 mL of MMA (molecular weight 100.12 and density 0.90). If C represents per cent conversion and t is time of polymerization of MMA, in minutes, then

$$C = \frac{w \times 100}{1 \times 0.90} \qquad \text{(b)}$$

From equations (a) and (b), R_p may be given as

$$R_p = \frac{0.90 \times C \times 10^3}{100 \times t \times 60 \times 100.12}$$

or, on simplification,

$$R_p = \frac{1.498 \times C \times 10^{-3}}{t} \qquad \text{(c)}$$

Thus, according to eq. (*c*), R_p may be evaluated from the slope of the plot of C versus time. In actual experiments, C has been obtained from a master graph plotted between volume contraction and per cent conversion. The per cent conversion (C) thus obtained was plotted against time (t) to calculate the rate of polymerization (R_p) (*cf.* Fig. 1).

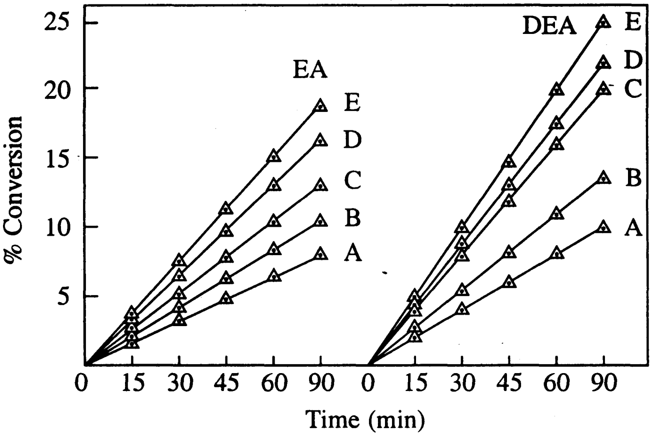


Fig. 1. Plots of % conversion versus time at 60°C for polymerization of [MMA] in DMSO medium and in presence of $PdCl_2$. [[EA] = 0.15 mol dm^{-3}, [DEA] = 0.10 mol dm^{-3}, [CCl_4] = 0.19 mol dm^{-3}, [$PdCl_2$] = 4.35×10^{-5} mol dm^{-3}, [MMA] = 0.85, 1.27, 1.69, 2.12 and 2.54 mol dm^{-3}, for A, B, C, D and E, respectively.]

The intrinsic viscosity (η_{int}) of the polymer was determined in chloroform solution with a Ubbelohde viscometer. The average degree of polymerization ($\bar{P}_n$) was calculated[5] using equation (d),

$$\eta_{int} = 1.91 \times 10^{-3}\bar{P}_n^{0.80} \tag{d}$$

which can be written as

$$\log \bar{P}_n = 1.25 \log (\eta_{int}) + 3.3986. \tag{e}$$

The molecular weight of polymer was obtained from viscometric data[6] using equation (f)

$$\eta_{int} = 4.8 \times 10^{-5}\bar{M}_n^{0.80} \tag{f}$$

RESULTS AND DISCUSSION

The rate of polymerization (R_p) of MMA at various reactant concentrations in presence of $PdCl_2$ (Table-1) or in presence of $RuCl_3$ (Table-2) has been evaluated. The monomer exponent value calculated from the slope of the linear plot between log (R_p) and log [MMA] (figure not given) was found to be *ca.* 1.0, suggesting a first order dependence of R_p on [MMA]. The first order variation of R_p with respect to MMA was further supported by the linear plot of R_p *vs.* [MMA].

TABLE-1

EFFECT OF [REACTANTS] ON R_p AT 60°C IN PRESENCE OF $PdCl_2$ IN DMSO MEDIUM

[MMA] (mol dm^{-3})	[EA] (mol dm^{-3})	or [DEA] (mol dm^{-3})	[CCl_4] (mol dm^{-3})	[$PdCl_2$] × 10^5 (mol dm^{-3})	$R_p \times 10^4$ (mol dm^{-3} s^{-1}) EA	DEA
0.64	0.15	0.10	0.19	4.35	0.95	1.40
0.85	0.15	0.10	0.19	4.35	1.50	1.85
1.27	0.15	0.10	0.19	4.35	1.95	2.50
1.69	0.15	0.10	0.19	4.35	2.80	3.75
2.12	0.15	0.10	0.19	4.35	3.40	4.30
2.54	0.15	0.10	0.19	4.35	3.90	5.00
1.69	0.04	0.05	0.19	4.35	1.50	2.25
1.69	0.08	0.15	0.19	4.35	1.87	3.95
1.69	0.22	0.20	0.19	4.35	3.15	4.70
1.69	0.29	0.25	0.19	4.35	3.75	5.35
1.69	0.37	0.30	0.19	4.35	4.10	5.80
1.69	0.15	0.10	0.10	4.35	1.50	2.00
1.69	0.15	0.10	0.38	4.35	3.75	4.20
1.69	0.15	0.10	0.58	4.35	4.10	4.30
1.69	0.15	0.10	0.80	4.35	4.30	4.55
1.69	0.15	0.10	0.98	4.35	4.50	4.85
1.69	0.15	0.10	0.19	Nil	1.00	2.20
1.69	0.15	0.10	0.19	2.20	2.20	3.25
1.69	0.15	0.10	0.19	8.70	3.40	4.25
1.69	0.15	0.10	0.19	13.05	4.15	4.75
1.69	0.15	0.10	0.19	17.40	4.50	5.15

TABLE-2
EFFECT OF [REACTANTS] ON R_p AT 60°C IN PRESENCE OF $RuCl_3$ IN DMSO MEDIUM

[MMA] (mol dm^{-3})	[EA] (mol dm^{-3})	or [DEA] (mol dm^{-3})	[CCl_4] (mol dm^{-3})	[$RuCl_3$] × 10^4 (mol dm^{-3})	$R_p \times 10^4$ (mol dm^{-3} s^{-1})	
					EA	DEA
0.78	1.45	0.91	0.18	2.10	0.93	1.31
1.18	1.45	0.91	0.18	2.10	1.49	2.05
1.57	1.45	0.91	0.18	2.10	1.68	2.43
1.97	1.45	0.91	0.18	2.10	2.24	2.99
2.36	1.45	0.91	0.18	2.10	2.62	3.55
1.57	1.45	0.91	0.18	Nil	0.45	1.25
1.57	1.45	0.91	0.18	2.10	1.68	2.43
1.57	1.45	0.91	0.18	4.20	2.43	3.12
1.57	1.45	0.91	0.18	6.30	2.80	3.40
1.57	1.45	0.91	0.18	8.40	3.18	3.75
1.57	1.45	0.91	0.18	10.50	3.37	4.20
1.57	0.72	0.45	0.18	2.10	1.12	1.74
1.57	1.45	0.91	0.18	2.10	1.68	2.43
1.57	2.18	1.37	0.18	2.10	1.87	2.74
1.57	2.91	1.82	0.18	2.10	2.24	3.24
1.57	3.64	2.28	0.18	2.10	2.80	3.55
1.57	1.45	0.91	0.18	2.10	1.68	2.43
1.57	1.45	0.91	0.36	2.10	2.05	3.05
1.57	1.45	0.91	0.54	2.10	2.43	3.60
1.57	1.45	0.91	0.72	2.10	2.99	4.15
1.57	1.45	0.91	0.90	2.10	3.18	4.70

R_p was measured at fixed concentrations of MMA, CCl_4 and catalyst (*i.e.*, palladium(II) or ruthenium(III)) and at varying concentrations of amino-alcohol (AA). R_p was always found to be proportional to $[AA]^{1/2}$ in presence of palladium(II) or ruthenium(III).

R_p increased with an increase in [$RuCl_3$] or [$PdCl_2$]. The plots of R_p versus $[RuCl_3]^{1/2}$ or $[PdCl_2]^{1/2}$ were linear with an intercept, suggesting that rate of polymerization of MMA is not negligible in absence of the catalyst. R_p values were also obtained in the absence of the catalyst (*i.e.*, when [$RuCl_3$] or [$PdCl_2$] = 0) and were found to be same as those obtained from the intercept of the plot of R_p versus $[PdCl_2]^{1/2}$ or $[RuCl_3]^{1/2}$.

In presence of ruthenium(III) (when [CCl_4]/[Aminoalcohol] ≤ 1), the plot of R_p versus $[CCl_4]^{1/2}$ was linear passing through origin, suggesting that R_p is proportional to $[CCl_4]^{1/2}$. In presence of palladium(II), an increase in R_p with an increase in [CCl_4] was observed at low CCl_4 concentrations. However, at higher

CCl_4 concentrations (when $[CCl_4]/[AA] > 1$) the rate of polymerization becomes independent of CCl_4 concentration.

The rate of polymerization was also studied at various temperatures, *viz.*, 50, 55, 60, 65 and 70°C (Table-3). The overall activation energies for polymerization of MMA by ethanolamine and diethanolamine evaluated from Arrhenius plot of log (R_p) versus (1/T) were found to be 64.0 ± 0.5 and 50.5 ± 0.5 kJ mol^{-1} respectively in presence of palladium(II) and 50 ± 0.5 and 54 ± 0.5 kJ mol^{-1} respectively in presence of ruthenium(III).

TABLE-3
EFFECT OF TEMPERATURE ON R_p IN DMSO MEDIUM

Temperature (°C)	$R_p \times 10^4$ mol dm^{-3} s^{-1}			
	in presence of $PdCl_2$ [a]		in presence of $RuCl_3$ [b]	
	EA	DEA	EA	DEA
50	1.25	1.70	0.93	1.60
55	1.90	2.80	1.31	2.14
60	2.80	3.75	1.68	2.43
65	3.75	4.15	2.05	3.49
70	4.15	4.60	2.62	4.10

[a] [EA] = 0.15 mol dm^{-3}, [DEA] = 0.10 mol dm^{-3}, $[CCl_4]$ = 0.19 mol dm^{-3}, $[PdCl_2] = 4.35 \times 10^{-5}$ mol dm^{-3} and [MMA] = 1.69 mol dm^{-3}.

[b] [EA] = 1.45 mol dm^{-3}; [DEA] = 0.91 mol dm^{-3}, $[CCl_4]$ = 0.18 mol dm^{-3}, $[RuCl_3] = 2.1 \times 10^{-4}$ mol dm^{-3} and [MMA] = 1.57 mol dm^{-3}

The polymerization of MMA was inhibited by hydroquinone (Table-4) indicating a free radical mechanism for the polymerization.

TABLE-4
EFFECT OF HYDROQUINONE ON THE RATE OF POLYMERIZATION OF MMA AT 60°C IN DMSO MEDIUM

[hydroquinone] (mol dm^{-3})	$R_p \times 10^4$ (mol dm^{-3} s^{-1}) in presence of $PdCl_2$ [a]		[hydroquinone] (mol dm^{-3})	$R_p \times 10^4$ (mol dm^{-3} s^{-1}) In presence of $RuCl_3$ [b]	
	EA	DEA		EA	DEA
Nil	2.81	3.75	Nil	1.68	2.43
0.0175	2.30	3.20	0.02	1.40	2.05
0.0350	1.70	2.10	0.04	1.10	1.75

[a] [EA] = 0.15 mol dm^{-3}, [DEA] = 0.10 mol dm^{-3}, $[CCl_4]$ = 0.19 mol dm^{-3}, $[PdCl_2] = 4.35 \times 10^{-5}$ mol dm^{-3} and [MMA] = 1.69 mol dm^{-3}.

[b] [EA] = 1.45 mol dm^{-3}, [DEA] = 0.91 mol dm^{-3}, $[CCl_4]$ = 0.18 mol dm^{-3}, $[RuCl_3] = 2.1 \times 10^{-4}$ mol dm^{-3} and [MMA] = 1.57 mol dm^{-3}.

The intrinsic viscosity (η_{int}) average degree of polymerization ($\bar{P}_n$) and molecular weight of polymers were obtained at different MMA concentrations and the results obtained in presence of $PdCl_2$ are reported in Table-5.

TABLE-5

η_{int}, MOLECULAR WEIGHT, $\bar{P}_n$ AND $k_p/k_t^{1/2}$ DATA FOR POLYMERIZATION OF MMA AT 25°C

Amine	[MMA] (mol dm^{-3})	η_{int}	$\bar{P}_n$	m.w.	$k_p/k_t^{1/2}$
Ethanolamine	0.85	0.44	896	89691	
	1.27	0.55	1191	118547	
	1.69	0.78	1830	183466	0.190
	2.12	0.95	2342	234742	
	2.54	1.09	2820	278753	
Diethanolamine	0.85	0.47	962	97400	
	1.27	0.60	1325	132168	0.230
	1.69	0.82	1953	195301	
	2.12	1.02	2558	256559	

[EA] = 0.15 mol dm^{-3}, [DEA] = 0.10 mol dm^{-3}, [CCl_4] = 0.19 mol dm^{-3}, and [$PdCl_2$] = 4.35 × 10^{-5} mol dm^{-3}

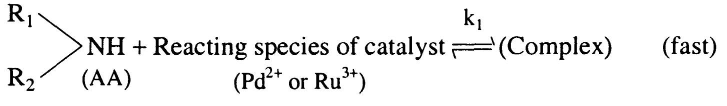
No polymerization of MMA was observed in absence of either aminoalcohol or CCl_4 under the present experimental conditions.

The polymerization of methylmethacrylate (MMA) initiated by amines or aminoalcohols in presence of CCl_4 has widely been studied by many investigators[7–9]. It has been observed that two different mechanisms for the initiation of polymerization of MMA involving charge transfer complex by the interaction of amine and CCl_4 (under the conditions $[CCl_4]/[Amine] \leq 1$) and by the interaction of amine and MMA (under the conditions $[CCl_4]/[Amine] > 1$) may be proposed. The charge transfer complex, so formed, is subsequently decomposed to produce $\overset{\bullet}{C}Cl_3$ species.

In some cases the formation of {transition metal ion (like Fe^{3+})-amine} complex and its reaction with CCl_4 to give $\overset{\bullet}{C}Cl_3$ during polymerization of monomer is also reported[10, 11].

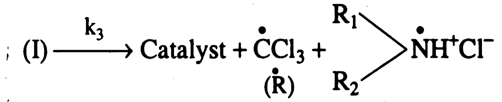
The complexes of platinum group metals are well known. Palladous chloride is quite soluble in hydrochloric acid and exists[12] as $[PdCl_4]^{2-}$. The various possible mononuclear complexes of palladium(II) with amine, phosphine, sulphide, etc. are reported in the literature[12]. The formation of palladous chloride complexes of aminoalcohols has also been confirmed during other investigation[13]. In dilute hydrochloric acid solution the $RuCl_3$ exists as $[Ru(H_2O)_6]^{3+}$. In very dilute HCl (0.01–0.80 mol dm^{-3}) the neutral form of the catalyst, *i.e.*, $RuCl_3$ has been considered[14] as the reacting species of the catalyst. The formation of ruthenium(III) complexes of aminoalcohols is also reported[15, 16].

Therefore, on the basis of above facts and experimental results, the mechanism for the initiation of the polymerization of MMA by aminoalcohols in presence of CCl_4 and catalyst ($PdCl_2$ or $RuCl_3$) may be proposed as follows,



$$\underset{(AA)}{\overset{R_1}{\underset{R_2}{>}}NH} + \underset{(Pd^{2+}\text{ or }Ru^{3+})}{\text{Reacting species of catalyst}} \overset{k_1}{\rightleftharpoons} \text{(Complex)} \quad \text{(fast)} \quad (1)$$

$$\text{(Complex)} + CCl_4 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{(Charge transfer complex)}}{\text{(I)}} \qquad \text{(slow)} \qquad (2)$$



$$\text{(I)} \xrightarrow{k_3} \text{Catalyst} + \underset{(\dot{R})}{\dot{C}Cl_3} + R_1R_2\dot{N}H^+Cl^- \qquad (3)$$

$$(\dot{R}) + \underset{\text{(MMA)}}{M} \xrightarrow{k_4} \dot{M}_1 \qquad \text{(Initiation)} \qquad (4)$$

where R_1 and R_2 represent —H, and —CH_2CH_2OH respectively in case of ethanolamine and —CH_2CH_2OH and —CH_2CH_2OH respectively in case of diethanolamine.

$R_1R_2\dot{N}H^+Cl^-$ formed in step (3) is expected to undergo dissociation in DMSO (a polar solvent) to give $R_1R_2\dot{N}H^+$ which may react with CCl_4 to produce $\dot{C}Cl_3$ and other products as reported by Takemoto and coworkers[17]. The termination step may also involve $\dot{C}Cl_3$ besides the bimolecular interaction of polymer radicals.

By applying the steady state conditions with respect to I, [I] may be obtained as

$$[I] = \frac{k_2[\text{Complex}][CCl_4]}{\{k_{-2} + k_3\}} \qquad (5)$$

or

$$[I] = \frac{k_2K_1[AA][\text{Catalyst}][CCl_4]}{\{k_{-2} + k_3\}} \qquad (6)$$

where [Complex] = K_1 [AA] [Catalyst] from step (1).

Since,

$$k_3[I] = k_4[\dot{R}][M] \qquad (7)$$

therefore, $[\dot{R}]$ may be given as

$$[\dot{R}] = \frac{k_3k_2K_1[AA][\text{Catalyst}][CCl_4]}{k_4[M]\{k_{-2} + k_3\}} \qquad (8)$$

The rate of initiation is given by

$$R_i = \frac{d[\dot{M}_1]}{dt} = k_4[M][\dot{R}]$$

On substituting the value of $[\dot{R}]$ from equation (8), the rate of initiation has been obtained as

$$R_i = \frac{K_1k_2k_3[AA][\text{Catalyst}][CCl_4]}{\{k_{-2} + k_3\}} \qquad (9)$$

Assuming bimolecular termination,

$$R_i = \frac{1}{k_t^{1/2}}\left[\frac{K_1k_2k_3[AA][\text{Catalyst}][CCl_4]}{\{k_{-2} + k_3\}}\right]^{1/2} \qquad (10)$$

The overall rate of polymerization R_p can be given as

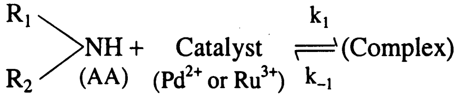
$$R_p = k_p \cdot [M]R_i \qquad (11)$$

and, therefore,

$$R_p = \frac{k_p}{k_t^{1/2}}\left[\frac{K_1k_2k_3}{\{k_{-2}+k_3\}}\right]^{1/2} [M][AA]^{1/2}[Catalyst]^{1/2}[CCl_4]^{1/2} \qquad (12)$$

The rate law (12) is in agreement with the observed results under the conditions when $[CCl_4]/[Amine] \leq 1$. The above rate law does not reflect the intercept of the plot of R_p versus $[PdCl_2]^{1/2}$ or $[RuCl_3]^{1/2}$ because the steps responsible for uncatalysed polymerization of MMA (already reported ref. 7 to 9) have not been included in the proposed mechanism for the palladium(II) or ruthenium(III) catalysed polymerization of MMA.

However, at higher CCl_4 concentrations (when $[CCl_4]/[AA] > 1$) the rate of polymerizaiton becomes independent of CCl_4 concentration. At low [aminoalcohol] and higher $[CCl_4]$ the steps (1) and (2) of the proposed mechanism may be considered as follows:



$$R_1R_2NH\ (AA) + Catalyst\ (Pd^{2+}\ or\ Ru^{3+}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (Complex) \qquad Slow \qquad (1a)$$

$$(Complex) + CCl_4 \xrightarrow{k_2} \underset{(Charge\ transfer\ complex)}{I} \qquad (fast) \qquad (2a)$$

By applying the steady state conditions with respect to complex, we get

$$[Complex] = \frac{k_1[AA][catalyst]}{\{k_{-1}+k_2[CCl_4]\}} \qquad (13)$$

and, therefore, $[\dot{R}]$ may obtained as,

$$[\dot{R}] = \frac{k_1k_2[AA][Catalyst][CCl_4]}{k_4[M]\{k_{-1}+k_2[CCl_4]\}} \qquad (14)$$

Thus taking the value of $[\dot{R}]$ from equation (14) in place of equation (8), the R_p is obtained as

$$R_p = \frac{k_p}{k_t^{1/2}}.[M][AA]^{1/2}[Catalyst]^{1/2}\left\{\frac{k_1k_2[CCl_4]}{k_{-1}+k_2[CCl_4]}\right\}^{1/2} \qquad (15)$$

However, at higher CCl_4 concentrations, $k_2[CCl_4] \gg k_{-1}$ may be taken as suitable approximation and, therefore, the equation (15) becomes

$$R_p = \frac{k_pk_1^{1/2}}{k_t^{1/2}} [M]^{1/2}[AA]^{1/2}[Catalyst]^{1/2} \qquad (16)$$

which is in agreement with the experimental results, *i.e.*, rate of polymerization is independent to CCl_4 at higher CCl_4 concentrations. As the palladium(II) or ruthenium(III) catalysed polymerization of MMA in presence of CCl_4 is initiated by free radical produced from the charge transfer complex, the following equation[8, 9] should be applicable,

$$-\bar{P}_n \frac{d[\mathrm{MMA}]}{dt} = \frac{k_p^2}{k_t}[\mathrm{MMA}]^2, \qquad (17)$$

where $\bar{P}_n$ is the degree of polymerization and $-d[\mathrm{MMA}]/dt = R_p$.

The plots of $R_p \cdot \bar{P}_n$ versus $[\mathrm{MMA}]^2$ were found to be in good agreement with equation (17). The values of $k_p/k_t^{1/2}$ obtained from the slopes of these plots were found to be 0.190 and 0.230 in case of ethanolamine and diethanolamine respectively and are comparable with easier reported values obtained for polymerization of MMA by aminoalcohols in absence of the catalyst[8, 9].

The experimental results, *i.e.*, first order dependence of the rate on monomer concentration in both the conditions, *i.e.*, when $[\mathrm{CCl_4}]/[\mathrm{Aminoalcohol}] < 1$ or $[\mathrm{CCl_4}]/[\mathrm{Aminoalcohol}] > 1$ and in presence of these catalysts, ruled out the possibility of involving charge transfer complex by interaction of aminoalcohol and monomer (MMA) as has been proposed during uncatalysed polymerization of MMA by aminoalcohols in presence of $\mathrm{CCl_4}$[8, 9]

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