

Kinetics and Mechanism of the Charge-Transfer Polymerization of Methyl Methacrylate Initiated with *n*-Butyl Amine and Carbon Tetrachloride Catalyzed by Palladium Dichloride

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ABSTRACT: We studied the kinetics and mechanism of the charge-transfer polymerization of methyl methacrylate (MMA) initiated with *n*-butyl amine (BA) and carbon tetrachloride (CCl₄) catalyzed by palladium dichloride (PdCl₂ or Pd^{II}) in a dimethyl sulfoxide medium by using a dilatometric technique at 60°C. The rate of polymerization (R_p) was a function of [MMA], [BA], [CCl₄], and [Pd^{II}]. The kinetic data indicated a mechanism involving the possible participation of the charge-transfer complex formed

between the {BA–Pd^{II}} complex and CCl₄ or monomer in the polymerization of MMA. In the absence of either CCl₄ or BA, no polymerization of MMA was observed under these experimental conditions. R_p was inhibited by hydroquinone; this suggested a free-radical initiation. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4025–4032, 2012

Key words: charge transfer; catalysts; kinetics (polym.)

INTRODUCTION

Platinum group metals have ability to form coordination and chelate complexes^{1,2} because of their stereochemistry and stabilities of different oxidation states. These complexes have been widely used as heterogeneous and homogeneous catalysts in various polymerizations^{3–6} and redox reactions.^{7–15} It has been observed that very small amounts of these metal ions ($\sim 10^{-6}$ M) are sufficient to accelerate the rate of polymerization (R_p) of monomers, namely, methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate,¹⁶ and acrylonitrile.¹⁷ These metal ions also help in the formation of charge-transfer complexes between amine/amino alcohols and carbon tetrachloride (CCl₄) or monomer and themselves; these play an important role in the initiation of the polymerization processes.

In the presence of platinum-group metals, the initiation of the polymerization of methyl methacrylate (MMA) initiated with an amine/amino alcohol and CCl₄ by a charge-transfer mechanism has been widely studied by many investigators.^{18,19} Two differ-

ent mechanisms for the initiation of the polymerization of MMA involving charge-transfer complexes have been proposed. These mechanisms are (1) the interaction²⁰ of amine and CCl₄ under the conditions $[\text{CCl}_4]/[\text{Amine}] \leq 1$ and (2) the interaction²¹ of amine and MMA under the conditions $[\text{CCl}_4]/[\text{Amine}] \geq 1$. Dass and coworkers^{22,23} and Dwivedi et al.²⁴ presented experimental evidence that both types of mechanisms are possible. Thus, the charge-transfer complex polymerization of MMA initiated by amine/amino alcohols and CCl₄ has been investigated with these mechanisms in detail by many investigators.^{25–35}

In this study, the kinetics and mechanism of the charge-transfer polymerization of MMA initiated with BA and CCl₄ and catalyzed by Pd^{II} in dimethyl sulfoxide (DMSO) medium were investigated. The effects of the reactant, MMA, BA, CCl₄, Pd^{II}, hydroquinone, temperature, and so on on R_p were studied. The systematic kinetic results are reported, and a mechanism of the polymerization process is proposed.

EXPERIMENTAL

Materials

The chemicals MMA (>99%), DMSO (>99.9%), CCl₄ (>99.9%), and BA (>96%) were purified before use. BA was distilled under reduced pressure under

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nitrogen.³⁶ CCl_4 was washed³⁷ with a dilute aqueous sodium carbonate solution and then with distilled water. The washed CCl_4 was dried over magnesium sulfate. The water that might have been present in DMSO was removed by azeotropic distillation with benzene. The product was then dried over calcium hydride and fractionally distilled under reduced pressure. The middle fraction of distilled DMSO was used for polymerization.³⁸ The stock solution of PdCl_2 was prepared by the dissolution of a 1.0-g sample of palladium dichloride in 25 mL of 0.01N hydrochloric acid (HCl) and then its dilution to 250 mL (with H_2O). Dilution of this stock solution was used as a catalyst. The PdCl_2 content of the stock solution was checked spectrophotometrically⁷ from time to time.

Polymerization procedure

The polymerization of MMA was carried out in a dilatometer (Custom build, MTU, MA, USA)³⁹ (bulb capacity = 5 mL, with an 11 cm long capillary with a 3-mm diameter) under a nitrogen atmosphere at 60°C with DMSO as the solvent. The required amounts of MMA, BA, CCl_4 , Pd^{II} , and DMSO were taken in the dilatometer, which was immediately sealed and placed in a thermostatic water bath maintained at $60 \pm 0.1^\circ\text{C}$ for 2 h. We monitored the progress of the reaction with the help of a cathetometer by recording the meniscus movement (i.e., volume per unit time). The polymerization was not allowed to proceed beyond 25% to prevent the formation of side products and to obtain reliable kinetic data. The polymer was precipitated with acidified methanol and dried to a constant weight.

Evaluation of R_p

R_p of MMA is given as

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

where w is the weight of polymer obtained from 1.0 mL of MMA (molecular weight = 100.12 g/mol and density = 0.94 g/cm³) and t is the time in minutes of polymerization of MMA. The percentage conversion (C) can be defined as follows:

$$C = \frac{w \times 100}{1 \times 0.94} \quad (2)$$

From eqs. (1) and (2), R_p may be given as

$$R_p = \frac{0.94 \times C \times 10^3}{100 \times t \times 60 \times 100.12}$$

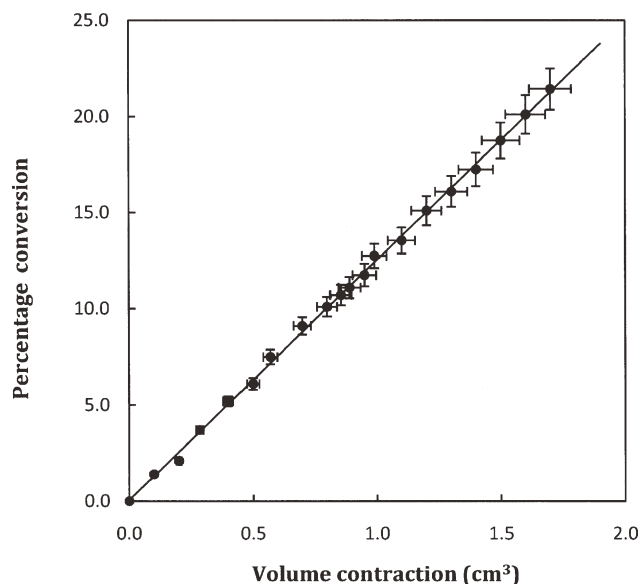


Figure 1 Master graph plotted between C versus volume contraction for Pd^{II} -catalyzed polymerization of MMA with BA and CCl_4 at 60°C in DMSO medium.

or on simplification

$$R_p = \frac{1.564 \times C \times 10^{-3}}{t} \quad (3)$$

Thus, according to eq. (3), R_p may be evaluated from the slope of the plot of C versus t . In actual experiments, C is obtained from a master graph plotted between C and volume contraction (Fig. 1). C thus obtained is plotted against t to calculate R_p .

Determination of the intrinsic viscosity ($[\eta]_{\text{int}}$) data

$[\eta]_{\text{int}}$ of the polymer was determined⁴⁰ in a chloroform solution with an Ubbelohde viscometer (Custom build, MTU, MA, USA) at 25°C. The viscometer was washed with chromic acid and then with distilled water and dried with acetone. Various solutions of polymer, namely, 0.1, 0.2, 0.3, 0.4, and 0.5 (w/v) in solvent, were prepared. The efflux time of these solutions in the Ubbelohde viscometer were determined with the help of a stopwatch. Equations (4) and (5) were used for calculate the specific viscosity ($[\eta]_{\text{sp}}$) and $[\eta]_{\text{int}}$, respectively:

$$[\eta]_{\text{sp}} = \frac{t - t_0}{t_0} \quad (4)$$

where t is the efflux time of solution and t_0 is the efflux time of the solvent.

$$[\eta]_{\text{int}} = \frac{[\eta]_{\text{sp}}}{C}$$

where $C \rightarrow 0$ and C is the concentration of the solution (wt %). $[\eta]_{\text{int}}$ was obtained from a graph plotted between $[\eta]_{\text{sp}}$ and C .

TABLE I
Effect of [MMA] and [BA] on R_p of the Pd^{II}-Catalyzed Polymerization of MMA at 60°C in DMSO Medium

[MMA] (mol/dm ³)	[BA] (mol/dm ³)	$R_p \times 10^4$ (mol dm ⁻³ s ⁻¹)
0.81	0.94	0.44 ± 0.01
1.32	0.94	0.85 ± 0.01
1.77	0.94	1.34 ± 0.03
2.64	0.94	1.76 ± 0.04
3.11	0.94	2.23 ± 0.07
3.54	0.94	2.68 ± 0.09
3.54	0.18	1.10 ± 0.02
3.54	0.37	1.60 ± 0.03
3.54	0.56	2.00 ± 0.05
3.54	0.75	2.40 ± 0.08
3.54	0.94	2.68 ± 0.09
3.54	1.13	2.95 ± 0.10
3.54	1.32	3.25 ± 0.11

$[\text{CCl}_4] = 0.77 \text{ mol/dm}^3$ and $[\text{PdCl}_2] \times 10^6 = 8.70 \text{ mol/dm}^3$.

Determination of the average degree of polymerization (\bar{P}_n)

\bar{P}_n was calculated⁴¹ with eq. (6), as follows:

$$[\eta]_{\text{int}} = 1.91 \times 10^{-3} \bar{P}_n^{0.80} \quad (5)$$

This can be written as

$$\log \bar{P}_n = 1.25 \log (\eta)_{\text{int}} + 3.3986 \quad (6)$$

Determination of the number-average molecular weight (\bar{M}_n) of the polymer

\bar{M}_n of the polymer was calculated⁴² with the Mark-Houwink equation [eq. (8)]:

$$[\eta]_{\text{int}} = K \bar{M}_n^\alpha \quad (7)$$

where $[\eta]_{\text{int}}$ is the intrinsic viscosity of the polymer (dL/g) and was measured at 25°C with the Ubbelohde viscometer. The values of the constants K and α used in eq. (7) were 4.8×10^{-5} and 0.80, respectively.

Equation (8) can be written as

$$[\eta]_{\text{int}} = 4.8 \times 10^{-5} \bar{M}_n^{0.80} \quad (8)$$

RESULTS AND DISCUSSION

The effects of the reactants, namely, MMA, BA, PdCl₂, hydroquinone, and temperature, on R_p of MMA were investigated. The kinetic results are summarized. No polymerization of MMA was observed in the absence of either BA or CCl₄ under

these experimental conditions; this suggested that presence of both BA and CCl₄ was necessary for the initiation of the polymerization of MMA.

The effect of MMA on R_p was measured at various initial concentrations of MMA at 60°C, with the concentrations of other reactants (viz., BA, CCl₄, and PdCl₂) kept constant. The results are given in Table I. The monomer exponent value calculated from the slope of the linear plot between $\log R_p$ and $\log [\text{MMA}]$ (Fig. 2) was found to be 1.00 ± 0.05 ; this indicated a first-order variation of R_p of MMA under the experimental conditions, that is, when $[\text{CCl}_4]/[\text{Amine}] \leq 1$.

The effect of BA on R_p was studied at various initial concentrations of BA at 60°C, with the concentrations of the other reactants (viz., MMA, CCl₄, and PdCl₂) kept constant. The results are given in Table I. The plot of $\log R_p$ versus $\log [\text{BA}]$ (Fig. 2) was linear, with a slope of about 0.5 ± 0.05 ; this suggested that R_p was proportional to $[\text{BA}]^{1/2}$.

R_p increased with increases in the concentration of CCl₄ or PdCl₂ (Table II) at fixed concentrations of the other reactants. The relationship between R_p and the concentration of CCl₄ or PdCl₂ was determined from the slope of the plot of $\log R_p$ versus $\log [\text{CCl}_4]$ (Fig. 3) or $\log R_p$ versus $\log [\text{PdCl}_2]$ (Fig. 4). The slope in each case was found to be approximately 0.5; this indicated the normal half-order dependence of R_p on $[\text{CCl}_4]$ or $[\text{Pd}^{\text{II}}]$.

The values of constant $[\eta]_{\text{int}}$, \bar{P}_n , and \bar{M}_n , obtained from eqs. (5), (6), and (8), respectively, are given in Table III. The experiments were also carried out at different concentrations of hydroquinone, and the rates of polymerization (R_p) are given in Table IV.

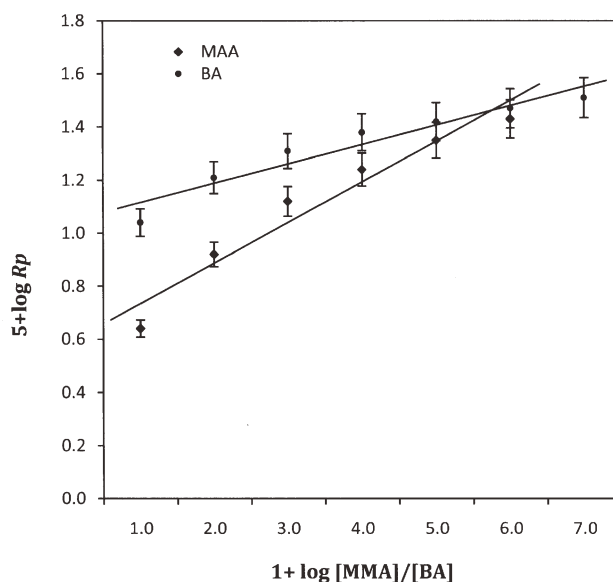


Figure 2 Plot of $\log R_p$ versus $\log [\text{MMA}]/[\text{BA}]$ for polymerization of MMA at 60°C in DMSO medium ($[\text{CCl}_4] = 0.77 \text{ mol/dm}^3$ and $[\text{PdCl}_2] = 8.70 \times 10^6 \text{ mol/dm}^3$).

TABLE II
Effect of $[\text{CCl}_4]$ and $[\text{PdCl}_2]$ on R_p of the Pd^{II} -Catalyzed Polymerization of MMA at 60°C in DMSO Medium

$[\text{CCl}_4]$ (mol/dm ³)	$[\text{PdCl}_2] \times 10^6$ (mol/dm ³)	$R_p \times 10^4$ (mol dm ⁻³ s ⁻¹)
0.19	8.70	0.67 ± 0.01
0.29	8.70	1.00 ± 0.02
0.38	8.70	1.33 ± 0.03
0.48	8.70	1.67 ± 0.03
0.58	8.70	2.00 ± 0.05
0.68	8.70	2.34 ± 0.07
0.77	8.70	2.68 ± 0.09
0.77	Nil	0.66 ± 0.01
0.77	4.35	1.80 ± 0.04
0.77	6.62	2.25 ± 0.06
0.77	8.70	2.68 ± 0.09
0.77	13.90	3.00 ± 0.10
0.77	15.22	3.20 ± 0.11

$[\text{MMA}] = 3.54 \text{ mol/dm}^3$ and $[\text{BA}] = 0.94 \text{ mol/dm}^3$.

Hydroquinone is a well-known retarder²⁴ of free-radical polymerization reactions, and it was observed that an increase in the concentration of hydroquinone decreased R_p in the presence of BA. This confirmed that the free-radical polymerization was operative in the system.

To obtain the activation parameters for the polymerization, R_p was determined at 50, 55, 60, and 65°C , and the results are given in Table IV. The activation parameters are given in Table V. The value of the energy of activation (E_a) and the pre-exponential constant ($\log A$) were evaluated from the slope of the Arrhenius plot of $\log R_p$ versus $1/T$. The enthalpy change (ΔH^\ddagger) was evaluated from E_a . The values of E_a and ΔH^\ddagger were found to be about 51.0 ± 1.0 and $62.0 \pm 1.0 \text{ kJ/mol}$, respectively.

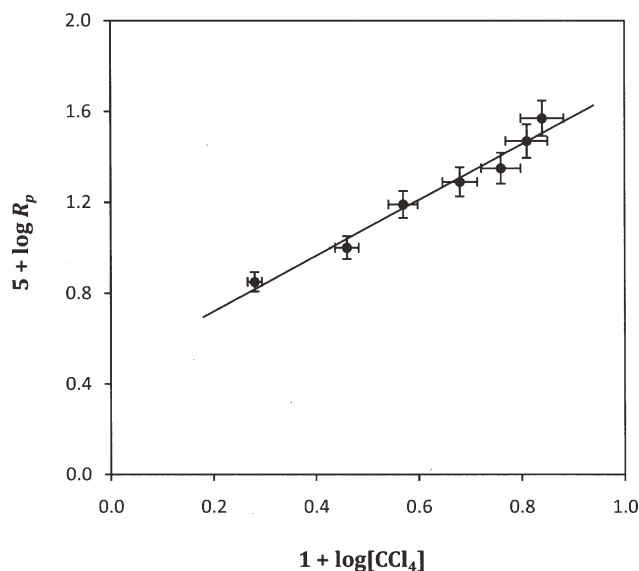


Figure 3 Plot of $\log R_p$ versus $\log [\text{CCl}_4]$ for the polymerization of MMA at 60°C in DMSO medium ($[\text{CCl}_4] = 0.77 \text{ mol/dm}^3$ and $[\text{PdCl}_2] = 8.70 \times 10^6 \text{ mol/dm}^3$).

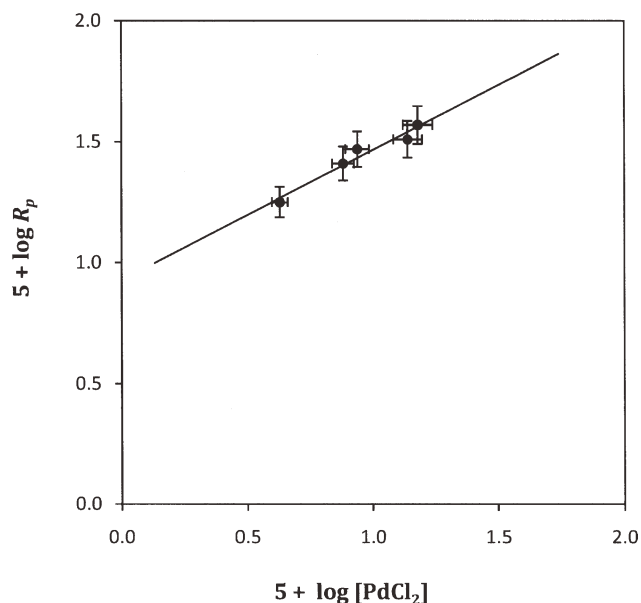


Figure 4 Plot of $\log R_p$ versus $\log [\text{PdCl}_2]$ for the polymerization of MMA at 60°C in DMSO medium ($[\text{CCl}_4] = 0.77 \text{ mol/dm}^3$ and $[\text{PdCl}_2] = 8.70 \times 10^6 \text{ mol/dm}^3$).

The negative entropy change (ΔS^\ddagger) of activation indicated the compactness of the prepared polymer in comparison to the monomer. The free-energy change (ΔG^\ddagger) indicated^{43,44} that the polymerization of MA in the presence of BA followed a similar mechanism. On the basis of the experimental results and reported literature, the mechanism for polymerization of MMA initiated by BA and CCl_4 with PdCl_2 as a catalyst was given.

Mechanism of polymerization

In Scheme 1, the first charge-transfer complexes (I_1 's), formed between the $\{\text{BA-Pd}^{\text{II}}\}$ complex and CCl_4 , and the second charge-transfer complexes (I_2 's), formed between the $\{\text{BA-Pd}^{\text{II}}\}$ complex and MMA, could not be detected in the polymerization system because they were too reactive. Therefore, we explored the Pd^{II} -catalyzed charge-transfer polymerization of MMA; the kinetics data indicated the

TABLE III
 $[\eta]_{\text{int}}$, \overline{P}_n , and \overline{M}_n Data for the Pd^{II} -Catalyzed Polymerization of MMA by BA in the Presence of CCl_4 at 25°C

$[\eta]_{\text{int}}$ (dL/g)	\overline{P}_n	$\overline{M}_n \times 10^5$
0.51 ± 0.01	911 ± 0.50	1.51 ± 0.01
0.62 ± 0.01	$1,701 \pm 0.5$	2.15 ± 0.01
0.71 ± 0.01	$2,517 \pm 1.0$	2.57 ± 0.05
0.80 ± 0.05	$3,421 \pm 1.0$	3.12 ± 0.05
0.87 ± 0.05	$4,117 \pm 1.5$	3.75 ± 0.07
0.95 ± 0.05	$4,921 \pm 1.0$	4.19 ± 0.09

$[\text{MMA}] = 3.54 \text{ mol/dm}^3$, $[\text{BA}] = 0.94 \text{ mol/dm}^3$, $[\text{CCl}_4] = 0.77 \text{ mol/dm}^3$, and $[\text{PdCl}_2] \times 10^6 = 8.70 \text{ mol/dm}^3$.

TABLE IV
Effect of [Hydroquinone] and Temperature on R_p of Pd^{II}-Catalyzed Polymerization of MMA in DMSO Medium

Temperature (°C)	[Hydroquinone] (mol/dm ³)	$R_p \times 10^4$ (mol dm ⁻³ s ⁻¹)
60	Nil	2.68 ± 0.09
60	0.018	2.10 ± 0.06
60	0.036	1.51 ± 0.03
60	0.94	1.76 ± 0.04
50	Nil	1.80 ± 0.04
55	Nil	2.55 ± 0.08
60	Nil	2.68 ± 0.09
65	Nil	3.20 ± 0.11

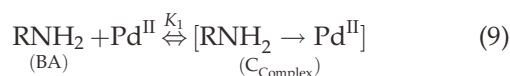
[MMA] = 3.54 mol/dm³, [BA] = 0.94 mol/dm³, [CCl₄] = 0.77 mol/dm³, and [PdCl₂] × 10⁶ = 8.70 mol/dm³.

possibility of formation of both the charge-transfer complex formed between the {BA-Pd^{II}} complex and CCl₄ and the other {BA-Pd^{II}} complex and MMA. On the basis of the experimental results and discussion, the mechanism for the Pd^{II}-catalyzed charge-transfer polymerization of MMA initiated with BA and CCl₄ in the presence of DMSO medium at 60°C is proposed, as given in Scheme 1.

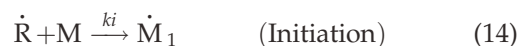
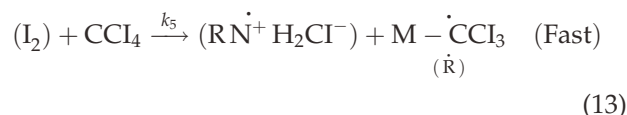
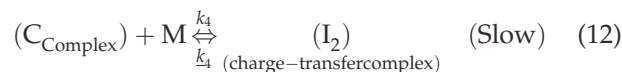
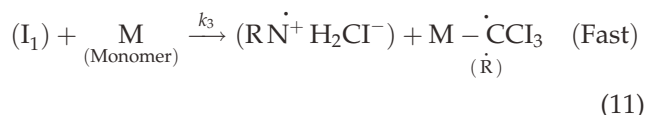
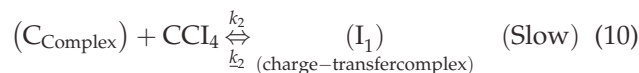
The polymerization of MMA was inhibited by hydroquinone; this indicated a free-radical mechanism for the polymerization. These free radicals were generated by the decomposition of the charge-transfer complex formed by EA as the electron donor.

The mechanism for the initiation of the polymerization of MMA by amino alcohol in the presence of CCl₄ under the experimental conditions [CCl₄]/[Amino alcohol] ≤ 1 and [CCl₄]/[Amino alcohol] ≥ 1 was explained⁴⁴ on the basis of formation of the charge-transfer complex by the interaction of the amino alcohol with CCl₄ and its subsequent decomposition to produce CCl₃. There have also been reports⁴⁵⁻⁴⁸ that the polymerization of amine/amino alcohol with CCl₄ systems is vastly accelerated by transition-metal ions, such as Fe³⁺ and Cu²⁺. In some cases, the formation of the {Fe³⁺-amine} complex and its reaction with CCl₄ to give CCl₃ has also been reported. The Pd^{II} complex with amines has also been observed during other kinetics investigations.^{49,50} Therefore, on the basis of the experimental results, the mechanism for the initiation of the Pd^{II}-catalyzed polymerization of MMA by BA in the presence of CCl₄ is proposed, as given in Scheme 1.

Initiation

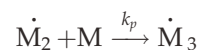


where C_{complex} and K₁ are Initiation complex and reaction rate constant, respectively,



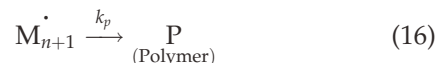
where K_i is the Initiation rate constant

Propagation



where K_p is the propagation rate constant

Termination



Scheme 1

where M^{+x} represents a metal complex with an oxidation state X, R represents the alkyl group of amine, and I₁ and I₂ represent the charge-transfer complexes. The RN⁺H₂Cl⁻ formed in step (11) and (12) was

TABLE V
Activation Parameters for the Pd^{II}-Catalyzed Polymerization of MMA Initiated with BA and CCl₄ in DMSO Medium

E_a (kJ/mol)	Log A	ΔH^\ddagger (kJ/mol)	$-\Delta S^\ddagger$ (J K ⁻¹ mol ⁻¹)	ΔG^\ddagger (kJ/mol)
51.0 ± 1.0	11.0 ± 0.5	62.0 ± 1.0	5.8 ± 0.5	75.0 ± 1.0

[MMA] = 3.54 mol/dm³, [BA] = 0.94 mol/dm³, [CCl₄] = 0.77 mol/dm³, and [PdCl₂] × 10⁶ = 8.70 mol/dm³.

expected to undergo dissociation in the polar solvent, that is, DMSO, to give $\text{RN}^+\text{H}_2\text{Cl}^-$, which reacted with CCl_4 to produce CCl_3 , as suggested by Takemoto et al.⁵¹

According to Scheme 1

$$[\text{C}_{\text{Complex}}] = K_1[\text{BA}][\text{Pd}^{\text{II}}] \quad \text{from step (1)} \quad (18)$$

By the application of steady-state condition with respect to $[\text{I}_1]$, we get

$$k_2[\text{C}_{\text{Complex}}][\text{CCl}_4] = k_2[\text{I}_1] + k_3[\text{I}_1][\text{M}]$$

Therefore, $[\text{I}_1]$ is obtained as

$$[\text{I}_1] = \frac{k_2[\text{C}_{\text{Complex}}][\text{CCl}_4]}{\{k_2 + k_3[\text{M}]\}} \quad (19)$$

On substituting the value of $[\text{C}_{\text{Complex}}]$ in eq. (19), we get

$$[\text{I}_1] = \frac{k_2K_1[\text{BA}][\text{Pd}^{\text{II}}][\text{CCl}_4]}{\{k_2 + k_3[\text{M}]\}} \quad (20)$$

Similarly, by applying steady-state condition with respect to $[\text{I}_2]$, we get

$$k_4[\text{C}_{\text{Complex}}][\text{M}] = k_4[\text{I}_2] + k_5[\text{I}_2][\text{CCl}_4]$$

Therefore, $[\text{I}_2]$ is obtained as

$$[\text{I}_2] = \frac{k_4[\text{C}_{\text{Complex}}][\text{M}]}{\{k_4 + k_5[\text{CCl}_4]\}} \quad (21)$$

On substituting the value of $[\text{C}_{\text{Complex}}]$ in eq. (21), we get

$$[\text{I}_2] = \frac{k_4K_1[\text{BA}][\text{Pd}^{\text{II}}][\text{M}]}{\{k_4 + k_5[\text{CCl}_4]\}} \quad (22)$$

If α is the fraction of $\text{C}_{\text{Complex}}$ used for the information of (I_1) , $(1 - \alpha)$ becomes the fraction used for the formation of I_2 , and the rate of formation (\dot{R}) is given as

$$\frac{d\dot{R}}{dt} = \alpha k_3[\text{I}_1][\text{M}] + (1 - \alpha)k_5[\text{I}_2][\text{CCl}_4] \quad (23)$$

On substituting the value of I_1 and I_2 from eqs. (20) and (22), respectively, in eq. (23), we get

$$\frac{d\dot{R}}{dt} = \frac{\alpha k_2 k_3 K_1 [\text{Pd}^{\text{II}}][\text{BA}][\text{CCl}_4][\text{M}]}{\{k_2 + k_3[\text{M}]\}} + \frac{(1 - \alpha)k_4 k_5 K_1 [\text{Pd}^{\text{II}}][\text{BA}][\text{CCl}_4][\text{M}]}{\{k_4 + k_5[\text{CCl}_4]\}} \quad (24)$$

If bimolecular termination is assumed, the rate of initiation (R_i) may be given as follows:

$$R_i = \frac{1}{k_t^{1/2}} \left[\frac{\alpha k_2 k_3 K_1 [\text{Pd}^{\text{II}}][\text{BA}][\text{CCl}_4][\text{M}]}{\{k_2 + k_3[\text{M}]\}} + \frac{(1 - \alpha)k_4 k_5 K_1 [\text{Pd}^{\text{II}}][\text{BA}][\text{CCl}_4][\text{M}]}{\{k_4 + k_5[\text{CCl}_4]\}} \right]^{1/2} \quad (25)$$

where k_t is the rate constant for the termination step.

The overall R_p can be expressed as

$$R_p = k_p[\text{M}]R_i \quad (26)$$

where k_p is the rate constant for the propagation step. On substituting the values of R_i , we get

$$R_p = \frac{k_p}{k_t^{1/2}} [\text{M}] \left[\frac{\alpha k_2 k_3 K_1 [\text{Pd}^{\text{II}}][\text{BA}][\text{CCl}_4][\text{M}]}{\{k_2 + k_3[\text{M}]\}} + \frac{(1 - \alpha)k_4 k_5 K_1 [\text{Pd}^{\text{II}}][\text{BA}][\text{CCl}_4][\text{M}]}{\{k_4 + k_5[\text{CCl}_4]\}} \right]^{1/2} \quad (27)$$

When the charge-transfer complex I_1 predominates, α may be taken as a unit, and eq. (27) reduces to

$$R_p = \frac{k_p}{k_t^{1/2}} (k_2 k_3 K_1)^{1/2} \frac{[\text{BA}][\text{Pd}^{\text{II}}]^{1/2} [\text{CCl}_4]^{1/2} [\text{M}]^{3/2}}{\{k_2 + k_3[\text{M}]\}^{1/2}} \quad (28)$$

Because step 3 is fast and $k_3[\text{M}] \gg k_2$, R_p may be given as

$$R_p = \frac{k_p}{k_t^{1/2}} (k_2 K_1)^{1/2} [\text{Pd}^{\text{II}}]^{1/2} [\text{BA}]^{1/2} [\text{CCl}_4]^{1/2} [\text{M}] \quad (29)$$

The experiment results were in agreement with eq. (29) under the conditions of $[\text{CCl}_4]/[\text{BA}] \leq 1$.

When I_2 predominates, α may be taken as zero, and eq. (27) reduces to

$$R_p = \frac{k_p}{k_t^{1/2}} (k_4 k_5 K_1)^{1/2} \frac{[\text{BA}]^{1/2} [\text{Pd}^{\text{II}}]^{1/2} [\text{CCl}_4]^{1/2} [\text{M}]^{3/2}}{\{k_4 + k_5[\text{CCl}_4]\}^{1/2}} \quad (30)$$

Because step (5) is fast and $k_5[\text{M}] \gg k_4$, R_p may be given as

$$R_p = \frac{k_p}{k_t^{1/2}} (k_4 K_1)^{1/2} [\text{Pd}^{\text{II}}]^{1/2} [\text{BA}]^{1/2} [\text{M}]^{3/2} \quad (31)$$

The rate law in eq. (31) explained the experimental results under the conditions $[\text{CCl}_4]/[\text{BA}] \geq 1$.

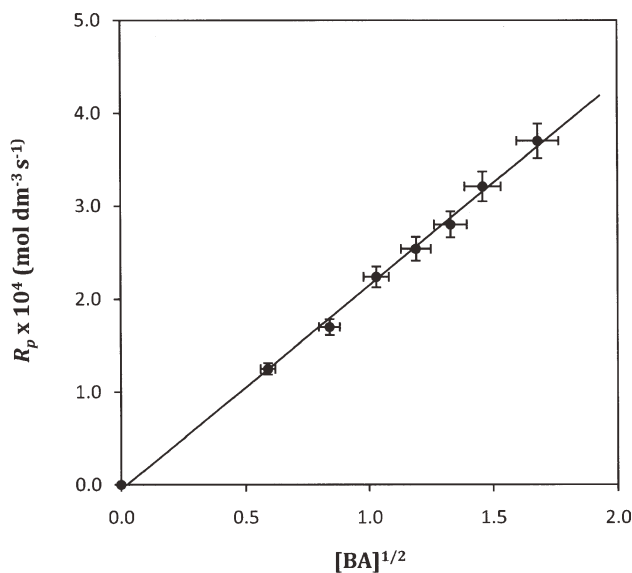


Figure 5 Plot of R_p versus $[BA]^{1/2}$ for the polymerization of MMA at 60°C in DMSO medium ($[CCl_4] = 0.77 \text{ mol/dm}^3$ and $[PdCl_2] = 8.70 \times 10^6 \text{ mol/dm}^3$).

Thus, the formation of charge-transfer complexes depended on the ratios $[CCl_4]/[BA] \leq 1$ and $[CCl_4]/[BA] \geq 1$, as observed earlier.

CONCLUSIONS

To confirm the validity of the rate law [eq. (31)], the plots of R_p versus $[BA]^{1/2}$, $[Pd^{II}]^{1/2}$, $[MMA]$, and $[CCl_4]^{1/2}$ were also obtained. The plot of R_p versus $[BA]^{1/2}$ (Fig. 5) was found to be linear, passing through the origin. The plot of R_p versus $[Pd^{II}]^{1/2}$ (Fig. 6) was linear with an intercept. The R_p value

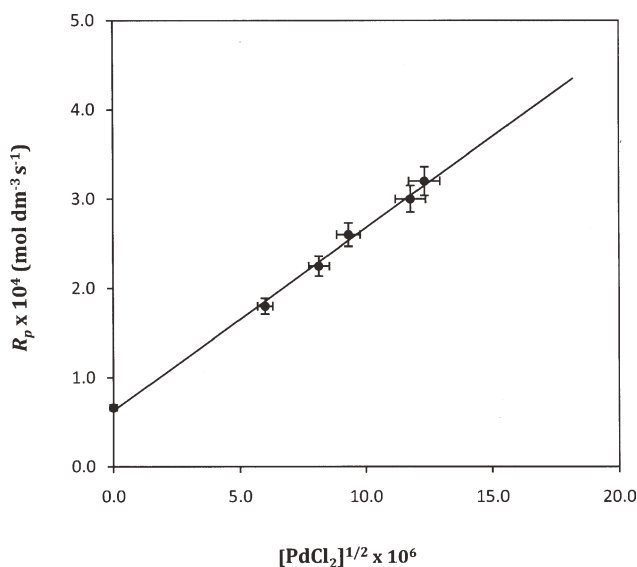


Figure 6 Plot of $\log R_p$ versus $[PdCl_2]^{1/2}$ for the polymerization of MMA at 60°C in DMSO medium ($[CCl_4] = 0.77 \text{ mol/dm}^3$ and $[PdCl_2] = 8.70 \times 10^6 \text{ mol/dm}^3$).

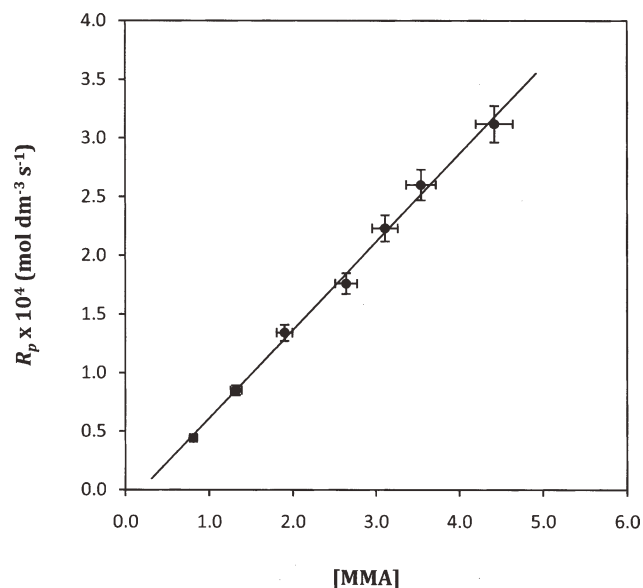


Figure 7 Plot of R_p versus $[MMA]$ for the polymerization of MMA at 60°C in DMSO medium ($[CCl_4] = 0.77 \text{ mol/dm}^3$ and $[PdCl_2] = 8.70 \times 10^6 \text{ mol/dm}^3$).

for the polymerization of MMA in the absence of Pd^{II} under these experimental conditions was also obtained and was found to be the same as that obtained from the intercept of the plot of R_p versus $[Pd^{II}]^{1/2}$. Thus, it was clear that the polymerization of MMA initiated by BA and CCl_4 also occurred in the presence of catalyst, as reported earlier.⁵² The rate law [eq. (31)] did not reflect the intercept of the plot of R_p versus $[Pd^{II}]^{1/2}$ (Fig. 6) because the steps responsible for the unanalyzed polymerization of MMA under these experimental conditions were not

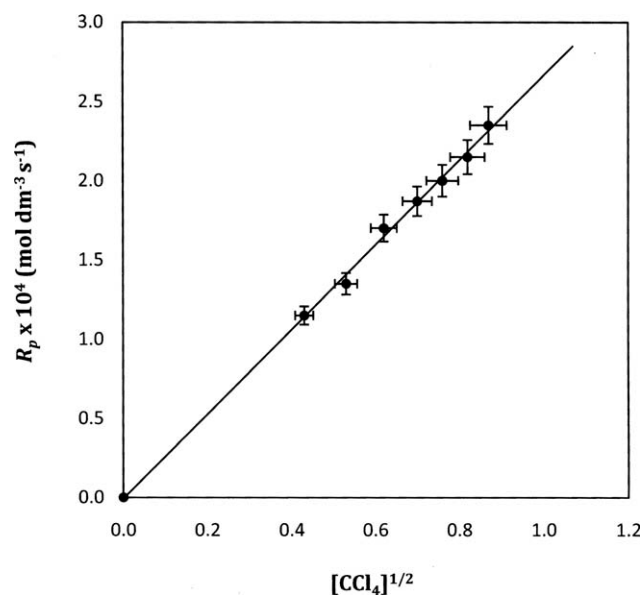


Figure 8 Plot of R_p versus $[MMA]$ for the polymerization of MMA at 60°C in DMSO medium ($[CCl_4] = 0.77 \text{ mol/dm}^3$ and $[PdCl_2] = 8.70 \times 10^6 \text{ mol/dm}^3$).

included in the proposed mechanism for the Pd^{II} - catalyzed polymerization of MMA.

However, the plot of R_p versus [MMA] (Fig. 7) and the plot of R_p versus $[\text{CCl}_4]^{1/2}$ (Fig. 8) intercepted in the [MMA] or $[\text{CCl}_4]^{1/2}$ axis. The mechanism of the uncatalyzed polymerization of MMA was explained on the basis of the formation of a charge-transfer complex between amine and MMA that initiated polymerization in the presence of CCl_4 . Thus, it was possible that MMA and CCl_4 up to these limiting concentrations were not free to initiate the polymerization of MMA under these experimental conditions.

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