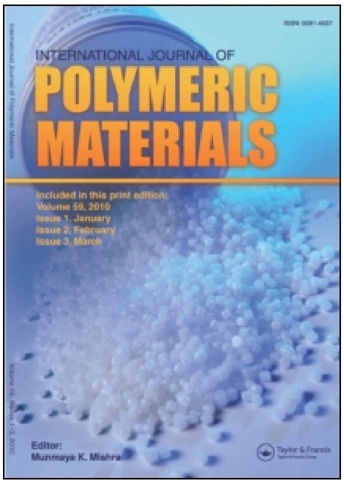


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Kinetics and Mechanism of Multi-site Phase Transfer Catalyzed Radical Polymerization of Ethyl Methacrylate

Murugesan Vajjiravel[a]; M. J. Umapathy[a]
[a] Department of Chemistry, College of Engineering, Anna University, Chennai, India

To cite this Article Vajjiravel, Murugesan and Umapathy, M. J.(2009) 'Kinetics and Mechanism of Multi-site Phase Transfer Catalyzed Radical Polymerization of Ethyl Methacrylate', International Journal of Polymeric Materials, 58: 1, 61 — 76

To link to this Article: DOI: 10.1080/00914030802462012

URL: http://dx.doi.org/10.1080/00914030802462012

International Journal of Polymeric Materials, 58:61–76, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030802462012

Taylor & Francis
Taylor & Francis Group

Kinetics and Mechanism of Multi-site Phase Transfer Catalyzed Radical Polymerization of Ethyl Methacrylate

Murugesan Vajjiravel and M. J. Umapathy
Department of Chemistry, College of Engineering, Anna University,
Chennai, India

The application of multi-site phase transfer catalyst (denoted herein as QX_2) with water-soluble initiator for the radical polymerization of ethyl methacrylate (EMA) was explored. The radical polymerization of water-insoluble vinyl monomer (EMA), with water – soluble initiator (potassium peroxydisulphate PDS) and a multi-site phase transfer catalyst (1,4-bis tributyl methyl ammonium) benzene dichloride TBMABDC) were carried out in a water/cyclohexane two-phase system at constant temperature $60 \pm 1°C$ under nitrogen circumstances. The rate of polymerization (Rp) was determined as a function of various reaction parameters such as the concentration of monomer, initiator, catalyst and variation of the aqueous phase and organic solvents and temperature. Based on the experimental results, a suitable kinetic scheme and mechanism has been proposed for the polymerization reaction.

Keywords: kinetics, multi-site phase transfer catalyst, radical polymerization, rate polymerization

INTRODUCTION

Phase-transfer catalysis (PTC) is a powerful tool in all branches of chemistry, which facilitates the interaction and chemical reaction between two or more chemical species located in immiscible phases [1–4]. In this technique, the reaction between chemical species is located in immiscible phases by the addition of a small quantity of phase transfer agent that extracts one of the reactants, most commonly an anion, across the interface into the other phase so that reaction can proceed. It offers operational simplicity, higher reaction

Received 7 August 2008; in final form 25 August 2008.

Address correspondence to M. Vajjiravel, Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea. E-mail: chemvel@rediffmail.com

rates, mild reaction conditions, the use of safe and inexpensive reagents and solvents, and addresses the opportunity to conduct reactions on large scale, safety and environmental concerns [5–8].

The concept of multi-sited phase transfer catalyst (QX_2) was introduced by Idoux et al. in which they have synthesized phosphonium and quaternary onium ions containing more than one active site per molecule [9]. Subsequently, a number of articles in multi-site phase transfer catalyst appeared in the literature [10–12]. However, the radical polymerizations of hydrophobic vinyl monomer using multi-site phase transfer catalyst have been less explored [13–16]. Hence, the present work endeavors to conduct a systematic investigation and explore the kinetics of free radical polymerization of ethyl methacrylate (EMA) using $K_2S_2O_8$ as a water-soluble initiator in the presence of multi-site phase transfer catalyst in cyclohexane/water two-phase system.

EXPERIMENTAL

Materials

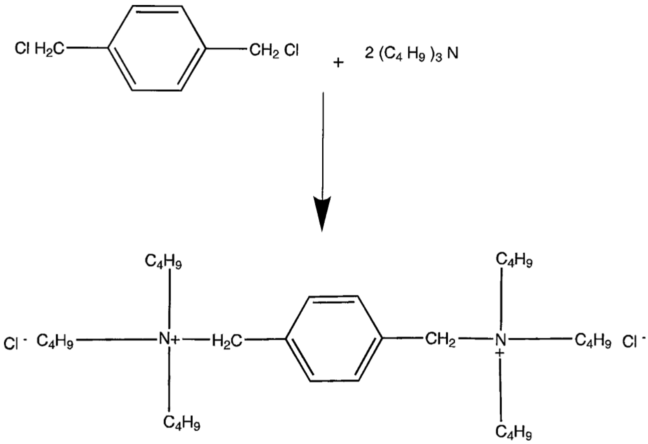
Ethyl methacrylate (Lancaster, Chennai, India), potassium peroxydisulphate (Merck, Mumbai, India) and methanol (SRL, Mumbai, India) were used as received. Distilled water and cyclohexane (SRL, Mumbai, India) were used as solvents for a two-phase system. The multi-site phase transfer catalyst, 1,4-bis(tributylmethylammonium)benzene-dichloride (TBMABDC) was synthesized by the following procedure.

Synthesis of Multi-site Phase Transfer Catalyst (QX_2)

One equivalent of α-α'dichloro-p-xylene (0.01 mol) was introduced into a 150 ml flask. Two equivalents of tributylamine (0.02 mol) dissolved in ethanol (30 ml) were then introduced to the flask for the reaction with α-α'dichloro-p-xylene under agitation speed of 600 rpm at 80°C for 60 h. The ethanol was stripped in a vacuum evaporator. White precipitates of 1,4-Bis(tributylmethylammonium)benzenedichloride was obtained. A white solid crystal of the products was obtained by recrystallizing the product in an ethanol solvent (Scheme 1) [14].

Polymerization of EMA

Polymerization reaction tubes contained equal volumes of aqueous phase and organic phase (10 ml each). The reaction mixture was thoroughly deaerated for 30 min. Then the reaction tube was placed in a



SCHEME 1 Synthesis of multi-site phase transfer catalyst (TBMABDC).

constant temperature water bath at constant temperature (60 ± 1°C) under unstirred condition. A known solution of PDS was added to the reaction mixture, polymerization occurred and poly (ethyl methacrylate) precipitated continuously for a definite time period. After the stipulated time period, each reaction was arrested by pouring the reaction mixture into ice–cold methanol containing traces of hydroquinone. The polymer was filtered through a sintered glass crucible, washed with methanol and distilled water, and then dried in vacuum oven at 50°C until constant weight was obtained. The rate of polymerization (Rp) was calculated from the weight of the polymer using the formula:

$$\mathrm{Rp} = 1000\,\mathrm{W/V \cdot t \cdot M}$$

where, W = weight of the polymer in gram, V = volume of the reaction mixture in ml, t = reaction time in seconds, M = molecular weight of the monomer.

Viscosity average molecular weight (M_v) of the polymer was determined in ethyl acetate at 30 ± 1°C with an Ubbelohde viscometer using the Mark-Houwink equation. From the molecular weight of the polymer, the degrees of polymerization ($\overline{P}_n$) values were calculated.

RESULTS AND DISCUSSION

Polymerization of ethyl methacrylate initiated by PDS QX_2 in cyclohexane/water two-phase system was studied under different

TABLE 1 Steady State Rate of Polymerization

Time (min)	$Rp \times 10^5\,mol \cdot dm^{-3}\,s^{-1}$
10	5.84
20	2.62
30	1.77
40	1.42
50	1.18
60	1.05

[EMA]: 2.0 $mol \cdot dm^{-3}$; [$K_2S_2O_8$]: 2.0 × $10^{-2}\,mol \cdot dm^{-3}$; [TBMABDC]: 2.0 × $10^{-2}\,mol \cdot dm^{-3}$ [H^+]: 0.5 $mol \cdot dm^{-3}$; [μ]: 0.2 $mol \cdot dm^{-3}$; Temp: 60 ± 1°C.

experimental conditions to evaluate the various reaction parameters influencing the polymerization reaction.

Steady State Rate of Polymerization

The steady state rate of polymerization for the ethyl methacrylate was studied by determining Rp at different intervals of time. The plot of Rp

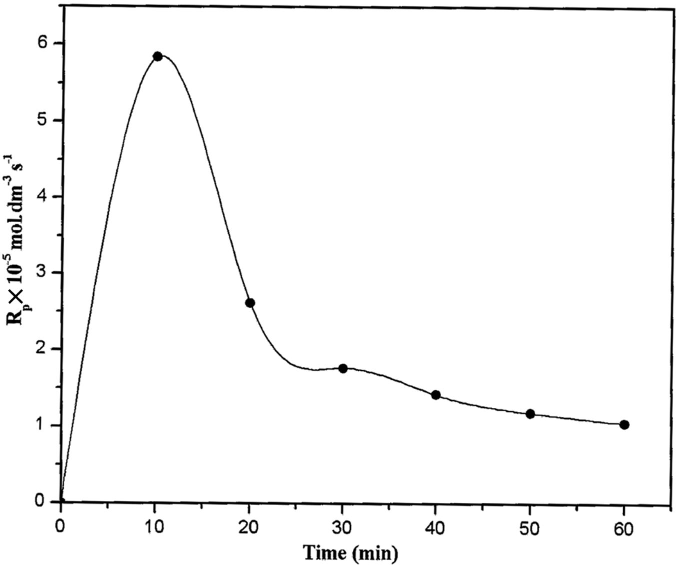


FIGURE 1 Steady state rate of polymerization reaction condition: [EMA]: 2.0 $mol \cdot dm^{-3}$; [$K_2S_2O_8$]: 2.0 × $10^{-2}\,mol \cdot dm^{-3}$; [TBMABDC]: 2.0 × 10^{-2} $mol \cdot dm^{-3}$] H^+]: 0.5 $mol \cdot dm^{-3}$; [μ]; 0.2 $mol \cdot dm^{-3}$; Temp: 60 ± 1°C.

vs. time shows that the steady state rate of polymerization of the ethyl methacrylate was obtained at 30 min. The polymerization reaction time was fixed for 30 min to carry out the experiments varying the other reaction parameters (Table 1, Figure 1).

Effect of [EMA] on Rp

The effect of monomer concentration on the rate of polymerization (Rp) was studied in the concentration range 4.5–9.5 mol dm^{-3} while keeping the concentrations of PDS, QX_2 ionic strength and pH constant. Rp increases with increased concentration of the EMA. The reaction order with respect to monomer concentration was determined from the plot of (6 + log Rp) vs. (3 + log [EMA]) and was found to be 0.50. Also the plot of Rp vs. [EMA] passing through the origin confirms the above observation (Table 2, Figure 2).

Effect of [PDS] on Rp

At fixed concentrations of other reaction parameters, the effect of concentration of $K_2S_2O_8$ on the rate of polymerization of EMA was studied in the range 1.5–2.5 mol dm^{-3}. Rp was found to increase with increasing concentration of $K_2S_2O_8$ in the EMA system. From the plot of (6 + log Rp) vs. (3 + log $K_2S_2O_8$]), the slope was found to be 1.0. A plot of Rp vs. [$K_2S_2O_8$] is linear passing through the origin, supporting the above deduction (Table 3, Figure 3).

Effect of [TBMABDC] on Rp

The effect of multi-site phase transfer catalyst [1,4-Bis(tributyl methyl ammonium) benzene dichloride (TBMABDC)] concentrations on the

TABLE 2 Effect of [EMA] on Rp

[EMA] $mol \cdot dm^{-3}$	$Rp \times 10^5$ $mol \cdot dms^{-3}\ s^{-1}$	3 + log [EMA]	6 + log [Rp]
4.5	1.9275	2.6532	1.2850
5.5	2.0701	2.7420	1.3160
6.5	2.3604	2.8129	1.3730
7.5	2.4043	2.8750	1.3810
8.5	2.5409	2.9294	1.4050
9.5	2.8353	2.9777	1.4526

[$K_2S_2O_8$]: 2.0×10^{-2} $mol \cdot dm^{-3}$; [TBMABDC]: 2.0×10^{-2} $mol \cdot dm$; [H^+]: 0.5 $mol \cdot dm^{-3}$; [μ]: 0.2 $mol \cdot dm^{-3}$; Temp: 60 ± 1°C.

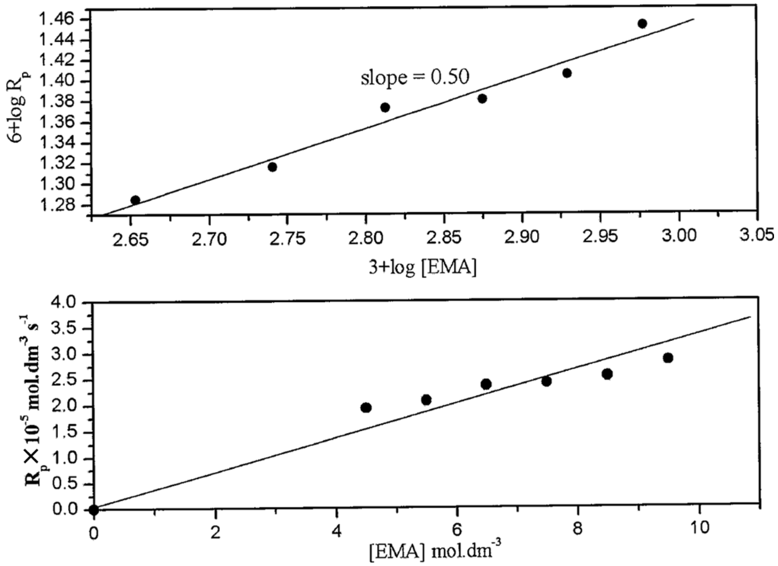


FIGURE 2 Effect of [EMA] on the Rp reaction condition: [$K_2S_2O_8$]: 2.0×10^{-2} mol · dm^{-3}; [TBMABDC]: 2.0×10^{-2} mol · dm^{-3}; [H^+]: 0.5 mol · dm^{-3}; [μ]: 0.2 mol · dm^{-3}; Temp: 60 ± 1°C.

rate of polymerization was studied by varying its concentration in the range of 1.5 to 2.5 mol dm^{-3} at fixed other reaction parameters. Rp increases with an increase in concentration of QX_2 and the results are plotted in Figure 4. From the slope of the linear plot obtained by plotting (6 + log Rp) vs. (3 + log [TBMABDC]), the order with respect to QX_2 was found to be 0.50. The observed order of 0.50 was confirmed from the straight line passing through the origin in a plot of Rp vs.

TABLE 3 Effect of [PDS] on Rp

[$K_2S_2O_8$] mol · dm^{-3}	Rp × 10^5 mol · dm^{-3} s^{-1}	3 + log [$K_2S_2O_8$]	6 + log Rp
1.5	1.2897	2.1760	1.1104
1.7	1.4621	2.2304	1.1650
1.9	1.5574	2.2787	1.1924
2.1	1.7764	2.3222	1.2495
2.3	2.1170	2.3617	1.3257
2.5	2.1978	2.3979	1.3420

[EMA]: 2.0 mol · dm^{-3}; [TBMABDC]: 2.0×10^{-2} mol · dm^{-2}; [H^+]: 0.5 mol · dm^{-3}; [μ]: 0.2 mol · dm^{-3}; Temp: 60 ± 1°C.

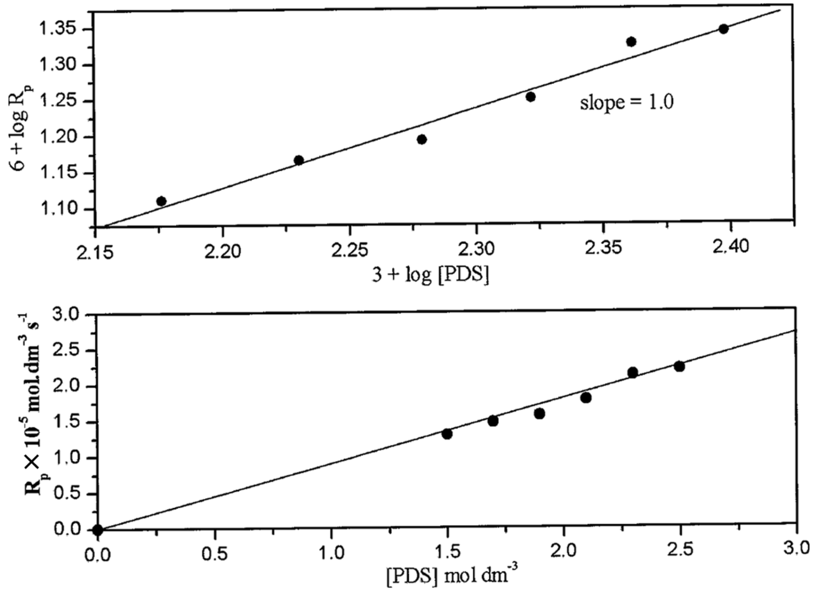


FIGURE 3 Effect of [PDS] on the Rp reaction condition: [EMA]: 2.0 mol · dm^{-3}; [TBMABDC]: 2.0 × 10^{-2} mol · dm^{-3}; [H$^+$]: 0.5 mol · dm^{-3}; [μ]: 0.2 mol · dm^{-3}; Temp: 60 ± 1°C.

[TBMABDC] (Figure 4, Table 4). Polymerization reaction did not occur in the absence of multi-site phase transfer catalyst even after several hours, which confirmed the role of QX_2 in the polymerization reaction.

Effect of Temperature on Rp

The effect of temperature was monitored by varying the temperature in the range of 50°C to 65°C at fixed concentration of other reaction parameters. The rate of polymerization increases with an increase in temperature. The activation energy (Ea) and other thermodynamic parameters, such as entropy of activation ($\Delta S^{\#}$), enthalpy of activation ($\Delta H^{\#}$) and free energy of activation ($\Delta G^{\#}$), have been calculated from the Arrehenius plot (Tables 5 and 6, Figure 5).

Effect of Volume Fraction of Aqueous Phase on Rp

Polymerization reactions were conducted with a constant volume of organic phase and different volumes of aqueous phase ($V_w/V_0 = 0.29$–0.90) at fixed concentrations of all other parameters. Little increase in rate of polymerization was observed with an increase

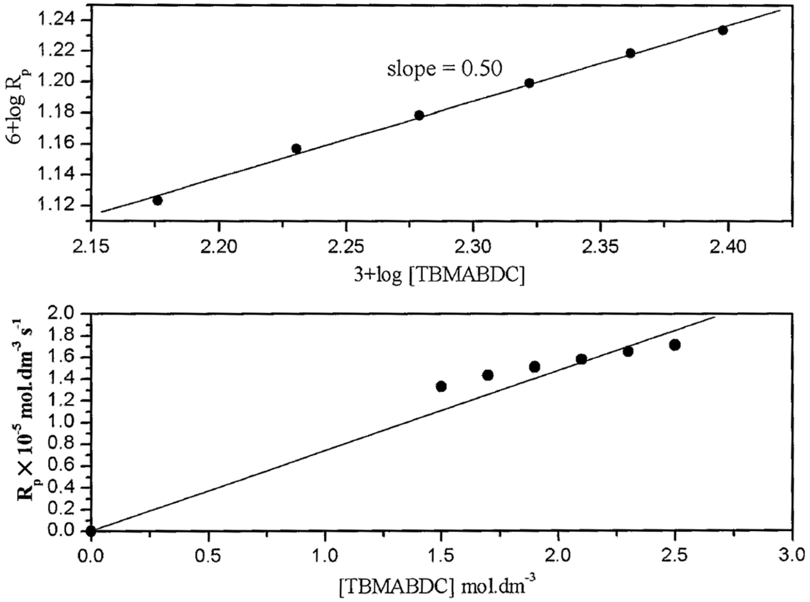


FIGURE 4 Effect of [TBMABDC] on the Rp reaction condition: [EMA]: $2.0\,\text{mol}\cdot\text{dm}^{-3}$; [$K_2S_2O_8$]: $2.0\times10^{-2}\,\text{mol}\cdot\text{dm}^{-3}$;[$H^+$]: $0.5\,\text{mol}\cdot\text{dm}^{-3}$; [μ]: $0.2\,\text{mol}\cdot\text{dm}^{-3}$; Temp: 60 ± 1°C.

in the volume of aqueous phase. From the plot of (6 + log Rp) vs. 1 + log (V_w/V_0) in Figure 6, the reaction order with respect to (V_w/V_0) was found to be 0.25 (Table 7).

Effect of Solvents' Polarity on Rp

The effect of solvents' polarity on Rp was examined by carrying out the polymerization reaction for ethyl methacrylate in three solvents,

TABLE 4 Effect of [TBMABDC] on Rp

[TBMABDC] $\text{mol}\cdot\text{dm}^{-3}$	$\text{Rp}\times10^5\,\text{mol}\cdot\text{dm}^{-3}\,\text{s}^{-1}$	3 + log [TBMABDC]	6 + log Rp
1.5	1.3280	2.1760	1.1232
1.7	1.4357	2.2304	1.1570
1.9	1.5087	2.2787	1.1786
2.1	1.5817	2.3222	1.1991
2.3	1.6547	2.3617	1.2187
2.5	1.7135	2.3979	1.2339

[EMA]: $2.5\,\text{mol}\cdot\text{dm}^{-3}$; [$K_2S_2O_8$]: $2.0\times10^{-2}\,\text{mol}\cdot\text{dm}^{-3}$; [$H^+$]: $0.5\,\text{mol}\cdot\text{dm}^{-3}$; [μ]: $0.2\,\text{mol}\cdot\text{dm}^{-3}$; Temp: 60 ± 1°C.

TABLE 5 Effect of Temperature on Rp

Temperature, K	$Rp \times 10^5 mol \cdot dm^{-3} s^{-1}$	$1/T \times lO^{-3}K^{-1}$	$5 + \log [Rp]$
323	1.1193	3.0960	1.0489
328	1.3627	3.0490	1.1344
333	1.4357	3.0030	1.1570
338	1.4844	2.9590	1.1715

[EMA]: $2.0 mol \cdot dm^{-3}$; [$K_2S_2O_8$]: $2.0 \times 10^{-2} mol \cdot dm^{-3}$; [TBMABDC]: 2.0×10^{-2} $mol \cdot dm^{-3}$ [H^+]: $0.5 mol \cdot dm^{-3}$; [μ] $0.2 mol \cdot dm^{-3}$; [μ]: 0.2 mole dm^{-3}.

cyclohexane, ethyl acetate and cyclohexanone, having the dielectric constants 2.02, 6.02, and 18.03, respectively. It was found that the Rp decreased in the following order:

Cyclohexanone > Ethylacetate > Cyclohexane

The increase in the rate of polymerization may be due to the increase in the polarity of the medium, which facilitates greater transfer of peroxydisulphate to the organic phase (Table 8).

Scheme 2 represents the reactions characterizing the polymerization of ethyl methacrylate (M) initiated by $K_2S_2O_8/QX_2$ in cyclohexane/water two-phase systems. It is assumed that dissociation of QX_2 (multi-site phase transfer catalyst) and $K_2S_2O_8$, formation of QS_2O_8 (complex of quaternary ammonium di-cation coupled with peroxy anion) in aqueous phase, and initiation of monomer in organic phase occur along the reactions Eqs. (l–5).

The equilibrium constants (K_1 and K_2) in the reactions in Eqs. (1–3) and distribution constants (α_1 and α_2) of QX_2 and QS_2O_8 are defined as follows, respectively.

$$K_1 = \frac{[Q^{2+}]_w[X^-]_w^2}{[QX]_w} \tag{6}$$

$$K_2 = \frac{[K^+]_w^2[S_2O_8^{2-}]_w}{[K_2S_2O_8]_w} \tag{7}$$

TABLE 6 Thermodynamic Parameters

Ea k J/mol	$\Delta G^{\#}$ k J/mol	$\Delta H^{\#}$ k J/mol	$\Delta S^{\#}$ k J/mol
16.40	69.01	28.33	−122.17

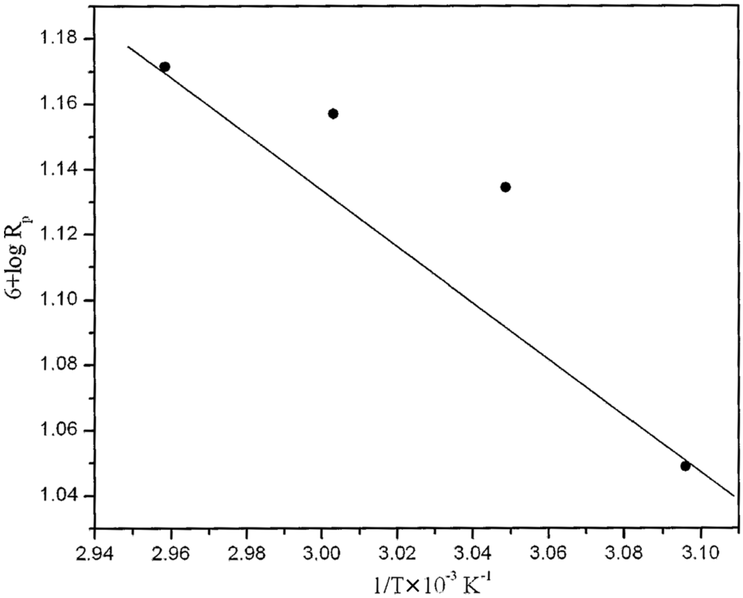


FIGURE 5 Effect of temperature on the Rp reaction condition: [EMA]: $2.0\,\text{mol}\cdot\text{dm}^{-3}$; [$K_2S_2O_8$]: $2.0\times10^{-2}\,\text{mol}\cdot\text{dm}^{-3}$; [TBMABDC]: $2.0\times10^{-2}\,\text{mol}\cdot\text{dm}^{-3}$ [H^+]: $0.5\,\text{mol}\cdot\text{dm}^{-3}$; [μ]: $0.2\,\text{mol}\cdot\text{dm}^{-3}$.

$$K_3 = \frac{[QS_2O_8]_w}{[Q^+]_w[S_2O_8^{2-}]_w} \tag{8}$$

$$\alpha_1 = \frac{[Q^{2+}X_2^-]_w}{[QX]_o} \tag{9}$$

$$\alpha_2 = \frac{[Q^{2+}S_2O_8^{2-}]w}{[QS_2O_8]_o} \tag{10}$$

The initiation rate (R_i) of radical, SO_4 in Eq. (4) may be represented as follows, f is initiator efficiency

$$R_i = \frac{d[SO_4]}{dt} = 2K_d fK_3[Q^{2+}]_w[S_2O_8^{2-}]_w \tag{11}$$

The growth of polymer chain according to the reaction in Eq. (5), the propagation step represented as follows:

$$\overset{0}{M}_1 + M \xrightarrow{Kp} \overset{0}{M}_n \tag{12}$$

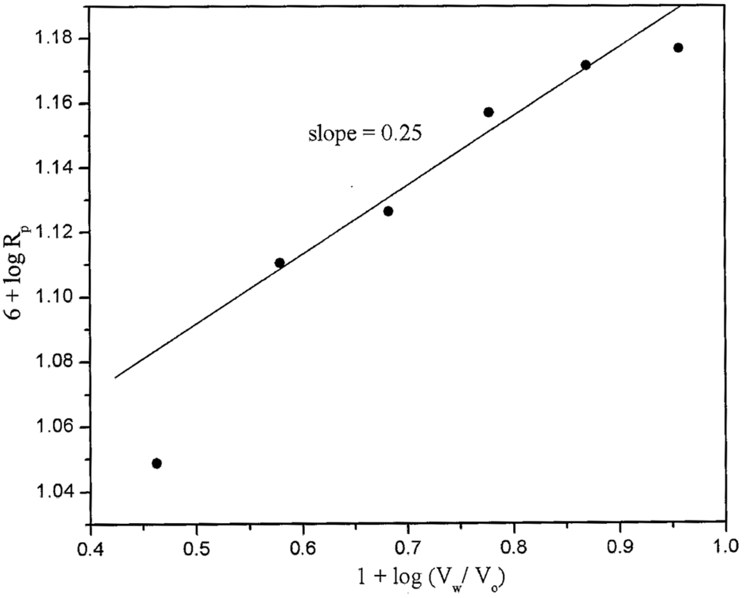


FIGURE 6 Effect of aqueous phase variation on the Rp reaction condition: [EMA]: 2.0 mol · dm^{-3}; [$K_2S_2O_8$]: 2.0 × 10^{-2} mol · dm^{-3}; [TBMABDC]: 2.0 × 10^{-2} mol · dm^{-3}[H^+]: 0.5 mol · dm^{-3}; [μ]: 0.2 mol · dm^{-3}; Temp: 60 ± 1°C.

$$\overset{0}{M}_{n-1} + M \xrightarrow{Kp} \overset{0}{M}_n \tag{13}$$

The rate of propagation (R_p) step in the reaction in Eq. (12) as

$$R_p = k_p[\overset{0}{M}][M] \tag{14}$$

TABLE 7 Effect of Aqueous Phase Volume on the Rp

V_w/V_0	$1 + \log(V_w/V_0)$	$R_p \times 10^{-5}$ mol · dm^{-3}S^{-1}	$6 + \log R_p$
0.29	0.4628	1.1193	1.0489
0.37	0.5789	1.2897	1.1104
0.48	0.6825	1.3383	1.1265
0.60	0.7781	1.4357	1.1570
0.73	0.8687	1.4844	1.1715
0.90	0.9565	1.5021	1.1766

[EMA]: 2.0 mol · dm^{-3}; [$K_2S_2O_8$]: 2.0 × 10^{-2} mol · dm^{-3}; [TBMABDC]: 2.0 × 10^{-2} mol · dm^{-3}. [H^+]: 0.5 mol · dm^{-3}; [μ]: 0.2 mol · dm^{-3}; Temp: 60 ± 1°C.

TABLE 8 Effect of Solvent Polarity on Rp

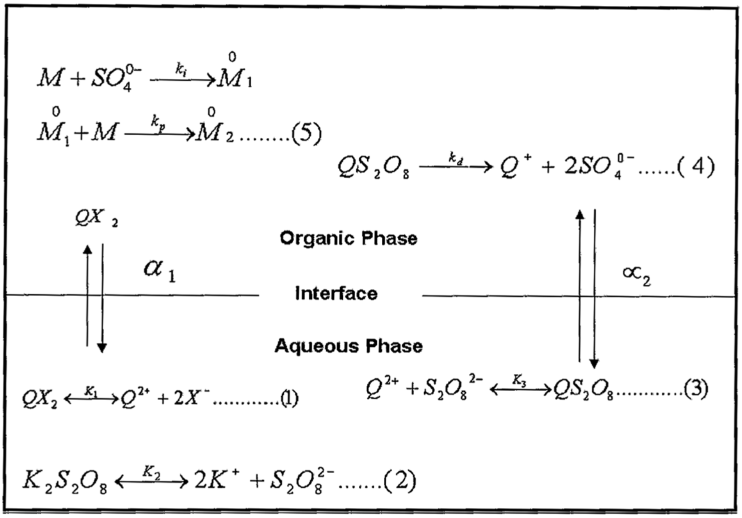
	$Rp \times 10^{-5}\,mol \cdot dm^{-3}\,S^{-1}$		
Experimental conditions	Cyclohexanone (18.3)	Ethylacetate (3.91)	Cyclohexane (1.13)
[EMA]: $2.0\,mol \cdot dm^{-3}$[$K_2\,S_2\,O_8$]: $2.0 \times 10^{-2}\,mol \cdot dm^{-3}$[TBMABDC] : $2.0 \times 10^{-2}\,mol \cdot dm^{-3}$ [H^+]: $0.5\,mol \cdot dm^{-3}$[μ]: $0.2\,mol \cdot dm^{-3}$ Temp: 60 ± 1°C.	1.55	1.48	1.38

$$[\overset{0}{M}] = \frac{R_p}{k_p[M]} \tag{15}$$

The termination occurs by the combinations of two growing polymer chain radicals, it can be represented as

$$2\,\overset{o}{M}_n \xrightarrow{k_t} polymer \tag{16}$$

The rate equation of termination(R_t) process according to Eq. (16)



SCHEME 2 Polymerization reaction pathways with multi-site phase transfer catalyst (QX_2) in an aqueous-organic two phase system.

$$R_t = 2k_t\left[\overset{o}{M}\right]^2 \tag{17}$$

The steady state prevails, the rate of initiation equals to rate of termination i.e.

$$R_i = R_t \tag{18}$$

$$2K_d f K_3[Q^{2+}]_w[S_2O_8^{2-}]_w = 2k_t\left[\overset{o}{M}\right]^2 \tag{19}$$

$$\left[\overset{o}{M}\right]^2 = \frac{K_d f K_3[Q^{2+}]_w[S_2O_8^{2-}]_w}{k_t} \tag{20}$$

$$\left[\overset{o}{M}\right] = \left[\frac{K_d f K_3[Q^{2+}]_w[S_2O_8^{2-}]_w}{k_t}\right]^{1/2} \tag{21}$$

Using Eqs. (15) and (21), the rate of polymerization is represented as follows

$$R_P = k_p\left[\frac{k_d K_3 f}{k_t}\right]^{1/2}[Q^{2+}]_w^{0.5}[S_2O_8^{2-}]_w^{l}[M]^{0.5} \tag{22}$$

The above equation satisfactorily explains all the experimental observations. The rate of polymerization (R_p) increses with increasing the concentration of EMA, PDS and multi-site phase transfer catalyst. The expression for the degree of polymerization is

$$\bar{P}_n = \frac{R_p}{R_t} \tag{23}$$

$$\overline{P}_n = \left[\frac{K_p[M]}{2(K_3 k_t k_d f)^{1/2}[Q^{2+}]_w^{0.5}[S_2O_8]_w^{1}}\right] \tag{24}$$

TABLE 9 EMA- TBMABDC -$K_2S_2O_8$ System: Degree of Polymerizatiion

[EMA]mol $\cdot$ dm^{-3}	$\bar{P}_n \times 10^{-3}$	$\frac{1}{\bar{P}_n} \times 10^{-3}$
0.5	6.57	0.15
1.0	4.45	0.22
1.5	3.32	0.30
2.0	2.20	0.45
2.5	1.75	0.57
3.0	1.60	0.62

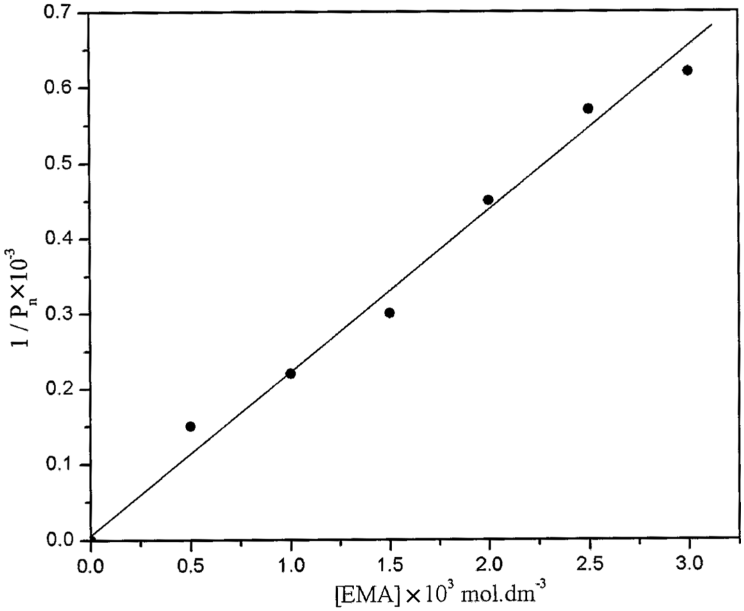


FIGURE 7 EMA-QX_2-$K_2S_2O_8$ System dependence of $\frac{1}{\bar{P}_n}$ on [EMA].

This Eq. (24) for the degree of polymerization $\bar{P}_n$ is directionally proportional to $[M]^{0.5}$. It is found that a plot of $\bar{P}_n$ versus $[M]^{0.5}$ gives straight line passing through the origin for ethyl methacrylate system (Table 9, Figure 7). This observation supported to the proposed mechanism.

CONCLUSIONS

Kinetics of radical polymerization of ethyl methacrylate were efficiently carried out using potassium peroxydisulphate (PDS) and multi-site phase transfer catalyst in aqueous-organic bi-phase system. The rate of polymerization (Rp) increases with increasing concentration of EMA, PDS and multi-site PTC. The Rp increases with increasing temperature and solvent polarity. From the study of kinetics, the orders with respect to EMA, PDS and multi-site PTC were found to be 0.50, 1.0 and 0.50, respectively. On the basis of kinetic study, a suitable kinetic scheme and mechanism have been proposed.

NOMENCLATURE

f	Efficiency of initiator
K_1	Equilibrium constant defined by Eq. (6)
K_2	Equilibrium constant defined by Eq. (7)
K_3	Equilibrium constant defined by Eq. (8)
k_d	Reaction rate constant of decomposition
k_i	Reaction rate constant of initiation
k_p	Reaction rate constant of propagation
k_t	Reaction rate constant of termination
Q^{2+}	Quaternary ammonium di-cation (multi-site PTC)
QX_2	Multi-site phase transfer catalyst
X^-	Halide ion of multi-site PTC
R_i	Rate of propagation defined by Eq. (11)
R_t	Rate of termination defined by Eq. (17)
R_p	Rate of polymerization defined by Eq. (22)
M	Monomer (ethyl methacrylate)
QS_2O_8	Complex of quaternary ammonium cation coupled with peroxy anion

Greek Letters

α_1	Distribution coefficient defined by Eq. (9)
α_2	Distribution coefficient defined by Eq. (10)

Subscripts

o	Organic phase
w	Aqueous phase

REFERENCES

[1] Starks, C. M., Liotta, C., and Halpern, M. (1994). *Phase Transfer Catalysis: Fundamentals, Applications and Industrial Perspectives*, Chapman and Hall, pp. 1, 452.

[2] Dehmlow, E. V. and Dehmlow, S. S. (1993). *Phase Transfer Catalysis*, VCH, Weinheim, pp. 1.

[3] Sasson, Y. and Neumann, R. (1997). *Handbook of Phase Transfer Catalysis*, Blackie Academic & Professional Edition, London, pp. 200.

[4] Jones, R. A. (2001). *Quaternary Ammonium Salts: Their Use in Phase Transfer Catalyzed Reactions*, Academic Press, UK, pp. 1.

[5] Albanese, D. *Cat. Rev.-Sci. Eng.* **45**, 369 (2003).

[6] Yang, H. M. and Wu, H. S. *Cat. Rev.-Sci. Eng.* **45**, 463 (2003).

[7] Jwo, J. J., *Cat. Rev.-Sci. Eng.* **45**, 397 (2003).

[8] Makosza, M. and Fedoryński, M. *Cat. Rev.-Sci. Eng.*, **45**, 321 (2003).

[9] Idoux, J. P., Wysocki, R., Young, S., Turcot, J., Ohlman, C., and Leonard, R., *Synth. Commun.* **13**, 139 (1983).

[10] Lissel, M., Feldman, D., Nir, M., and Rabinovitz, M., *Tetrahedron. Let.* **30**, 1683 (1989).

[11] Balakrishnan, T. and Jayachandran, J. P., *Synth. Commun.* **25**, 3821 (1995).
[12] Wang, M. L. and Hsieh, Y. M., *J. Mol. Catal. A. Chemical.* **210**, 59 (2004).
[13] Vajjiravel, M., Umapathy, M. J., and Bharathbabu, M., *J. Appl. Polym. Sci.* **105**, 3634 (2007).
[14] Vajjiravel, M. and Umapathy, M. J., *J. Polym. Res.* **15** (1), 27 (2008).
[15] Vajjiravel, M. and Umapathy, M. J., *J. Polym. Res.* **15** (3), 235 (2008).
[16] Vajjiravel, M. and Umapathy, M. J., *Colloid. Polym. Sci.* 286, 729 (2008).