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ORIGINAL CONTRIBUTION

Free radical polymerisation of methyl methacrylate initiated by multi-site phase transfer catalyst—a kinetic study

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Abstract The kinetics of multi-site phase transfer catalysed (MPTC) radical polymerisation of methyl methacrylate (MMA) using potassium peroxydisulphate (PDS) and synthesised 1, 4-Bis (tributyl methyl ammonium) benzene dichloride (TBMABDC) as multi-site phase transfer catalyst was investigated in cyclohexane–water two-phase system at constant temperature 60±1 °C under nitrogen circumstances. The role of concentrations of monomer, initiator, catalyst and volume fraction of aqueous phase, solvent polarity and temperature on the rate of polymerisation (Rp) was ascertained. The order with respect to monomer, initiator and phase transfer catalyst were found to be 0.80, 1.0 and 0.5, respectively. A suitable kinetic scheme has been proposed to account for the experimental observations and its significance is discussed. The prepared polymer was characterised by spectral analysis.

Keywords Kinetics · Multi-site phase transfer catalyst · Radical polymerisation

Introduction

Phase transfer catalysis (PTC) was first introduced in the 1960s as a convenient and significantly useful tool for accelerating the reactions between the chemical reactants located in immiscible phases that generally do not have a solvent has become common exercise in recent years. PTC methodology involves a substrate (which is soluble in organic phase) and a reagent (which is dissolved in the aqueous phase). The substrate and the reagent are then brought together by a phase transfer catalyst, which transports the reagent into the organic phase where the reaction can take place with the substrate. There are several advantages of the PTC system over single systems, such as acceleration of the rate under mild reaction conditions; use of inexpensive, recoverable and non-toxic solvents; a lower reaction temperature and the use of water together with an organic solvent as reaction medium.

In general, PTC is an efficient methodology for the synthesis of a variety of compounds, such as haloalkanes, alkenes, aliphatic nitro compounds, nitriles, azides, sulphides, organo–metallic compounds, pharmaceuticals, amino acids, epoxides, peptides, pesticides and polymers. It has found widespread applications not only in research laboratories but also in numerous industrial processes [1–5]. Many authors reported the single-site PTC assisted radical polymerisation of hydrophobic vinyl monomers in aqueous–organic two phase system [6–13]. The first report published on multi-site phase transfer catalyst was by Idoux et al., and they have synthesised phosphonium and quaternary onium ions containing more than one site per molecule [14].

The literature survey reveals that, so far, few reports are available in multi-site phase transfer catalyst assisted radical polymerisation of vinyl monomers. However, recently, we have reported the multi-site PTC assisted radical polymerisation of acrylonitrile in an aqueous–organic two-phase system [15]. Consecutively, this stimulated us to explore the kinetics of free radical polymerisation of methyl methacrylate (MMA) using potassium peroxydisulphate (PDS) as water soluble initiator and 1, 4-Bis (tributyl methyl ammonium) benzene dichloride (TBMABDC) as multi-site phase transfer catalyst in cyclohexane/water biphase media.

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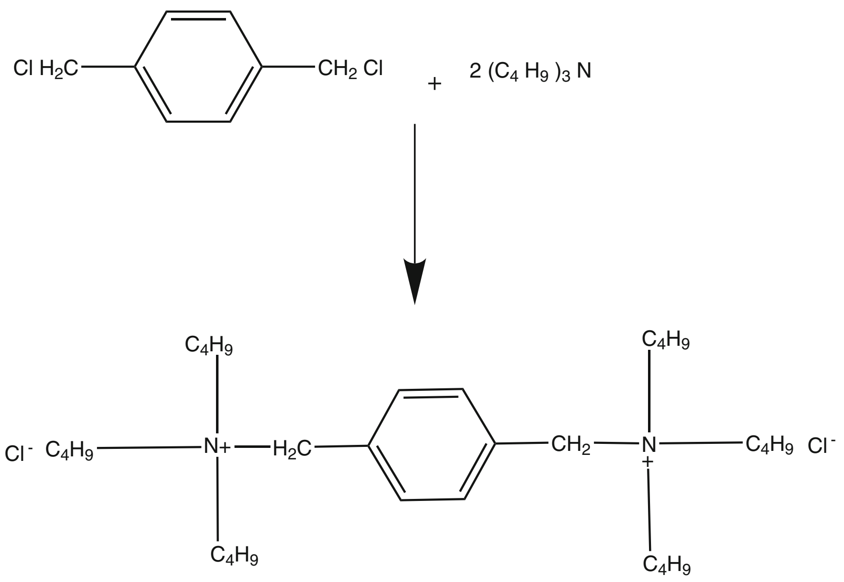
Scheme 1 Synthesis of multi-site phase transfer catalyst



Experimental

Materials

MMA (Lancaster, Chennai, India), PDS (Merck, Mumbai, India), cyclohexane (CDH, New Delhi, India) and methanol (SRL, Mumbai, India) were used as received. The multi-site phase transfer catalyst TBMABDC was synthesised by the following procedure.

Synthesis of multi-site phase transfer catalyst

Measured quantity of 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) was then introduced in the flask for the reaction with α-α′ dichloro-p-xylene under an agitation speed of 600 rpm at 80 °C for 60 h. Organic solvent ethanol was stripped in a vacuum evaporator. White precipitates of TBMABDC were obtained. A white solid crystal of the product is obtained by recrystalling the product in an ethanol solvent (Scheme 1) [16].

Table 1 Steady-state rate of polymerisation

Time (min)	$Rp\times10^5$, mol dm^{-3} s^{-1}
10	0.275
20	0.378
30	0.586
40	1.090
50	0.972
60	0.945
70	0.958
80	0.935

Reaction condition: [MMA], 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 °C

Polymerisation procedure

The polymerisation reactions were carried out in Pyrex glass tubes provided with inlets and outlets for nitrogen. The reaction mixture consists of equal volumes of aqueous phase and organic phase. The monomer in cyclohexane was the organic phase. The catalyst, sodium bisufate (for adjusting the ionic strength [μ]) and sulphuric acid (for maintaining the [H^+]) were taken in the aqueous phase. The reaction mixture was thoroughly deaerated for 30 min. All reactions were carried out at 60±1 °C. When PDS was added to the reaction

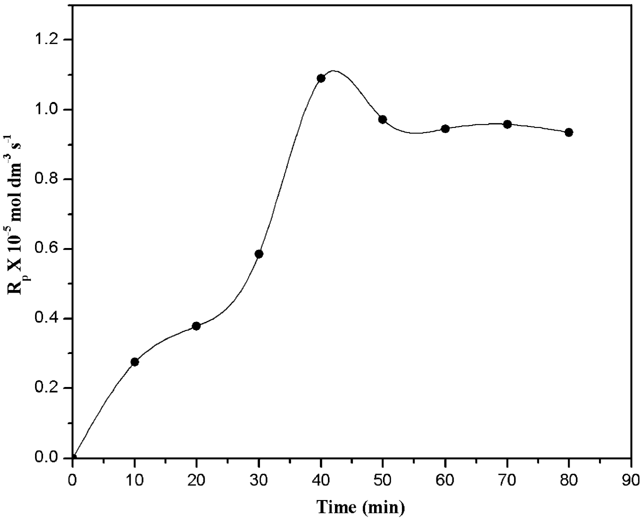


Fig. 1 Steady state rate of polymerisation. Reaction condition: [MMA], 2.0 mol dm^{-3}; [K2S2O8], 2.0×10^{-2} mol dm^{-3}; [MPTC], 2.0×10^{-2} mol dm^{-3}; [H+], 0.5 mol dm^{-3}; [μ], 0.2 mol dm^{-3}; Temp, 60±1 °C

Table 2 Effect of monomer concentration on Rp

[MMA] mol dm^{-3}	Rp×10^{5} mol dm^{-3} s^{-1}	3+log [MMA]	6+log [Rp]
4.5	0.2122	2.6532	0.3267
5.5	0.2330	2.7420	0.3617
6.5	0.2413	2.8129	0.3825
7.5	0.2871	2.8750	0.458
8.5	0.3038	2.9294	0.4825
9.5	0.4078	2.9777	0.6104

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 °C

Table 3 Effect of PDS concentration 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	0.6998	2.1760	0.8450
1.7	0.9885	2.2304	0.9950
1.9	1.0693	2.2787	1.0291
2.1	1.1668	2.3222	1.0670
2.3	1.1776	2.3617	1.0710
2.5	1.2445	2.3979	1.0950

Reaction condition: [MMA], 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 °C

mixture, polymerisation occurred, and polymethyl methacrylate precipitated continuously during polymerisation. The reactions were 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 a vacuum oven at 50 °C. The rate of polymerisation (Rp) was calculated from the weight of the polymer formed.

Rp was calculated from the weight of polymer obtained using the formula

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

where

W Weight of the polymer in grams
V Volume of the reaction mixture in milliliters
T Reaction time in seconds
M Molecular weight of the monomer

Instruments

Viscosity average molecular weight (M_v) of the polymer was determined in benzene at 30±1° C with an Ubbelohde viscometer using Mark–Houwink equation [17]. From the molecular weight of the polymer, the degrees of polymerisation ($\bar{P}_n$) values were calculated. The Fourier transform infrared (FT-IR) spectrum of poly(methyl methacrylate) was recorded on a FT-IR spectrometer (Perkin Elmer RX I) in the spectral region from 4,000 to 500 cm^{-1}. Pellets of about 40 mg KBr powder containing fine powder of the polymer sample were made before recording. The ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian 100 HA JEOL 400 MHz spectrometer by using $CDCl_3$ as a solvent and tetramethylsilane as an internal reference.

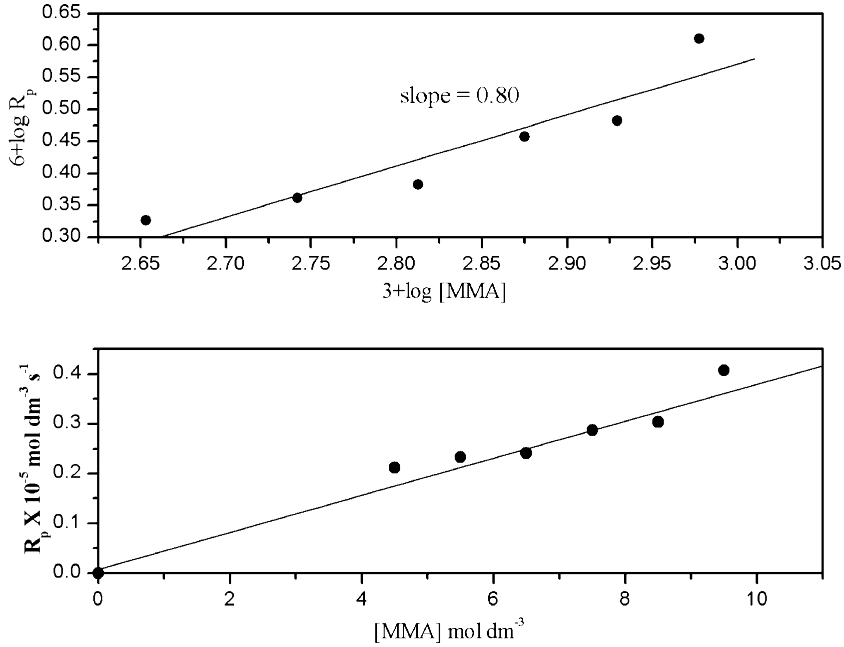


Fig. 2 Effect of monomer concentrations on the Rp. Reaction condition: [K2S2O8], 2.0×10^{-2} mol dm^{-3}; [MPTC], 2.0×10^{-2} mol dm^{-3}; [H+], 0.5 mol dm^{-3}; [μ], 0.2 mol dm^{-3}; Temp, 60±1 °C

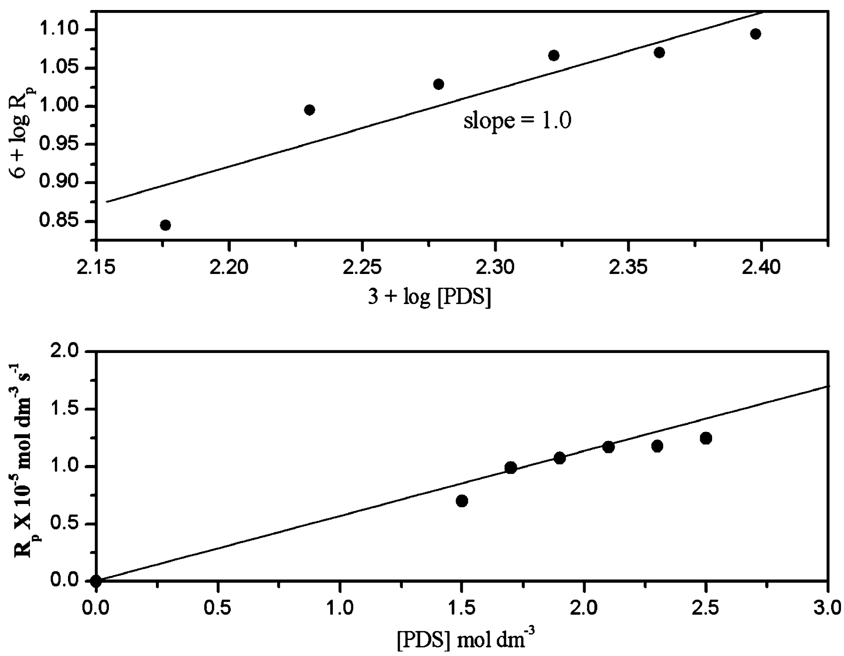


Fig. 3 Effect of Initiator concentrations on the Rp. Reaction condition: [MMA], 2.0 mol dm^{-3}; [MPTC], 2.0×10^{-2} mol dm^{-3}; [H+], 0.5 mol dm^{-3}; [μ], 0.2 mol dm^{-3}; Temp, 60±1 °C

Results and discussion

The polymerisation of MMA initiated by PDS-multi-site phase transfer catalysed (MPTC) in cyclohexane/water biphase was studied under different experimental conditions to evaluate the various parameters, which influence the polymerisation reaction.

Steady state rate of polymerisation

The steady state rate of polymerisation for the MMA was studied by determining Rp at different intervals of time. The plot of Rp vs time shows that the steady state rate of polymerisation of the MMA was obtained at 40 min. The polymerisation reaction time was fixed for 40 min to carry out the experiments with variation of other parameters (Table 1, Fig. 1).

Table 4 Effect of MPTC concentration on Rp

[TBMABDC] mol dm^{-3}	Rp×10^5 mol dm^{-3} s^{-1}	3+log [TBMABDC]	6+log Rp
1.5	0.9053	2.1760	0.9568
1.7	0.9649	2.2304	0.9845
1.9	0.9808	2.2787	0.9916
2.1	1.0315	2.3222	1.0135
2.3	1.1127	2.3617	1.0464
2.5	1.1792	2.3979	1.0716

Reaction condition: [MMA], 2.5 mol dm^{-3} ; [$K_2S_2O_8$], 2.0×10^{-2} mol dm^{-3} ; [H^+], 0.5 mol dm^{-3} ; [μ], 0.2 mol dm^{-3} ; Temp, 60 °C.

Effect of monomer concentration on Rp

The effect of concentration on the rate of polymerisation (Rp) was studied at various concentrations of monomers from 4.5 to 9.5 mol dm^{-3} keeping the concentration of PDS, MPTC, ionic strength and pH constant. Rp increases with increase in the concentration of the monomer. The reaction order with respect to monomer concentration was determined from the plot of (6+log Rp) vs (3+log [MMA]), and it was found to be 0.80. Also, the plot of Rp vs [MMA] passing through the origin confirms the above observations (Table 2, Fig. 2).

Effect of PDS concentration on Rp

The rate of polymerisation increased with an increase in concentration of PDS ($K_2S_2O_8$) (1.5–2.5-mol dm^{-3}) at fixed reaction condition. Rp was found to increase with increasing concentration of $K_2S_2O_8$. From the plot of (6+log Rp) vs (3+log [$K_2S_2O_8$]), the slope is found to be 1.0. The plot of Rp vs [$K_2S_2O_8$] is linear passing through the origin supporting the above deduction (Table 3, Fig. 3).

Effect of PTC concentration on Rp

The effect of concentration of multi-site phase transfer catalyst TBMABDC on the rate of polymerisation was studied by varying its concentration in the range from 1.5 to 2.5 mol dm^{-3} at fixed concentrations of other parameters. Rp increases with an increase in concentration of MPTC. The plot of (6+log Rp) vs (3+log [MPTC]) was found to

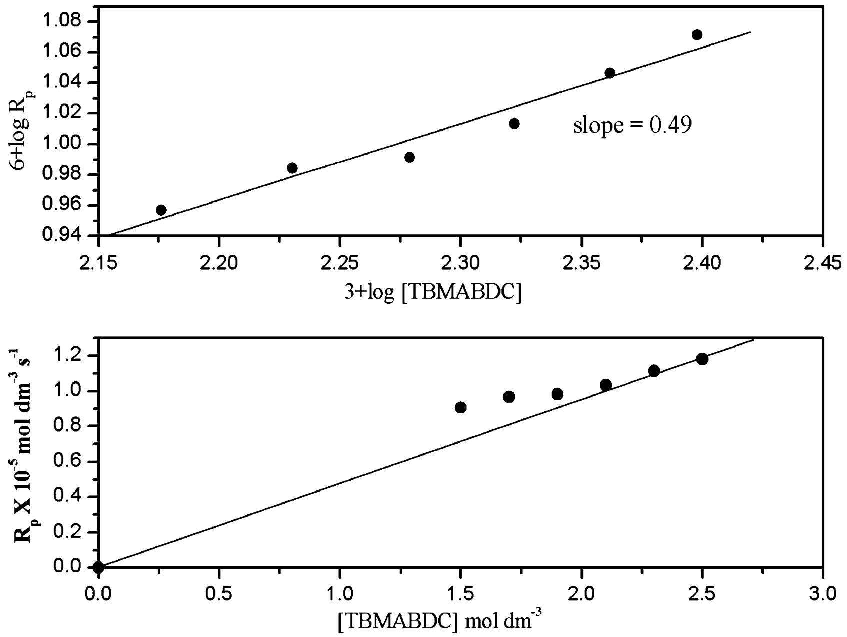


Fig. 4 Effect of MPTC concentrations on the Rp. Reaction condition: [MMA], 2.0 mol dm^{-3}; [K2S2O8], 2.0×10^{-2} mol dm^{-3}; [H+], 0.5 mol dm^{-3}; [μ], 0.2 mol dm^{-3}; Temp, 60±1 °C

be 0.49. The plot of Rp vs [MPTC] passing through origin confirms the above observations (Table 4, Fig. 4). The half order with respect to catalyst has already been reported in the phase transfer catalyst assisted polymerisation of vinyl monomers [9, 10]. In the absence of phase transfer catalyst, no reaction occurred, which confirmed the role of PTC in the reaction.

Effect of temperature on Rp

The effect of temperature was monitored by varying the temperature in the range of 50 to 65 °C and keeping other reaction parameters constant. The rate of polymerisation increases with an increase in temperature. The overall activation energy of polymerisation (Ea) obtained from plot of log Rp vs 1/T is 29.10 kJ mol^{-1} for the MMA system (Table 5, Fig. 5). The 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 value of activation energy (Table 6).

Table 5 Effect of temperature on Rp

Temperature, K	Rp×10^5 mol dm^{-3} s^{-1}	1/T×10^{-3} K^{-1}	5+log [Rp]
323	0.7585	3.0960	0.8805
328	0.9280	3.0490	0.9675
333	1.0900	3.0030	1.0374
338	1.2276	2.9590	1.0890

Reaction condition: [MMA], 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}

Effect of acid (H^+) and ionic strength (μ) on Rp

The variation in acid and ionic strength had no significant changes in the rate of polymerisation.

Effect of volume fraction of aqueous phase on Rp

Polymerisation reactions were conducted with a constant volume of organic phase and different volumes of aqueous phase (V_w/V_o=0.29–0.90) at fixed concentrations of all other parameters. A small increase in rate of polymerisation was observed with an increase in the volume of the aqueous phase. From the plot of (6+log Rp) vs 1+log (V_w/V_o) in

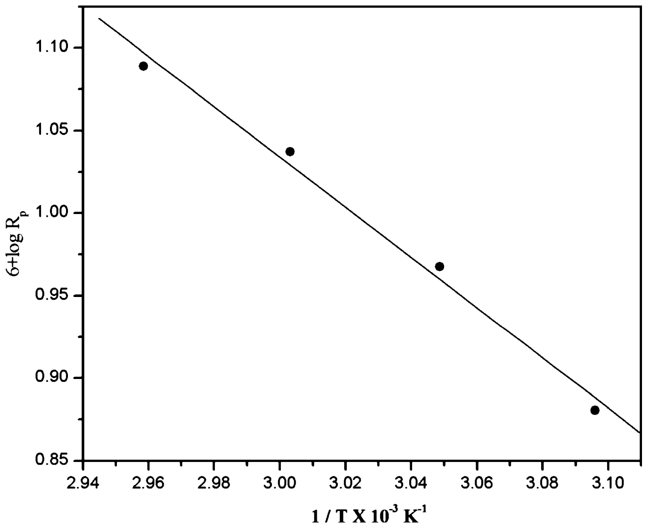


Fig. 5 Effect of temperature on the Rp. Reaction condition: [MMA], 2.0 mol dm^{-3}; [K2S2O8], 2.0×10^{-2} mol dm^{-3}; [PTC], 2.0×10^{-2} mol dm^{-3}; [H+], 0.5 mol dm^{-3}; [μ], 0.2 mol dm^{-3}

Table 6 Thermodynamic parameters

Ea k J/mol	$\Delta G^{\#}$ k J /mol	$\Delta H^{\#}$ k J/mol	$\Delta S^{\#}$ k J /mol
29.10	69.99	45.76	−72.77

Fig. 6, the reaction order with respect to (V_w/V_o) was found to be 0.020 (Table 7).

Effect of solvents polarity on Rp

The effect of solvent on Rp was examined by carrying out the polymerisation reaction for MMA in three solvents, cyclohexane, ethylacetate 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 polymerisation may be due to the increase in the polarity of the medium, which facilitates greater transfer of peroxydisulphate to the organic phase (Table 8).

Mechanism and rate law

Scheme 2 represents the reactions characterising the polymerisation of MMA (M) initiated by $K_2S_2O_8$/MPTC in cyclohexane/water two-phase systems. It is assumed that dissociation of QX and $K_2S_2O_8$, formation of QS_2O_8 in aqueous phase and initiation of monomer in organic phase occurs along the reactions such as Eqs. 1–5.

The equilibrium constants (K_1 and K_2) in the reactions in Eqs. 1–3 and distribution constants (a_1 and a_2) of QX and QS_2O_8 are defined as follows, respectively:

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

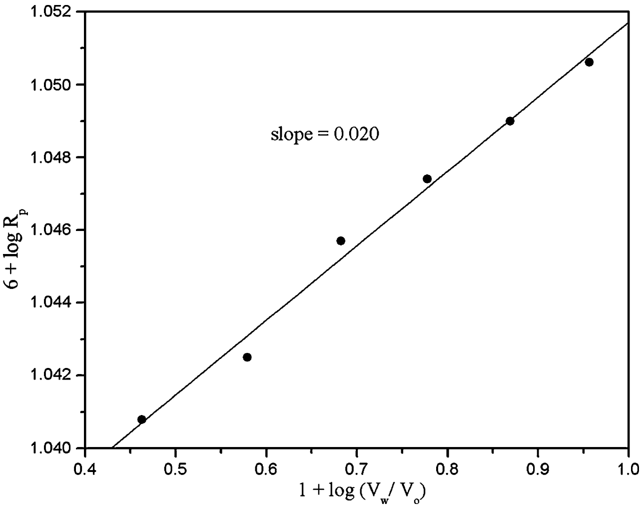


Fig. 6 Effect of aqueous phase variation on the Rp

Table 7 Effect of aqueous phase volume on the Rp

V_w/V_o	1+log (V_w/V_o)	$R_p\times10^5$ mol dm^{-3} S^{-1}	6+log R_p
0.29	0.4628	1.0986	1.0408
0.37	0.5789	1.1028	1.0425
0.48	0.6825	1.1111	1.0457
0.60	0.7781	1.1153	1.0474
0.73	0.8687	1.1194	1.0490
0.90	0.9565	1.1236	1.0506

Reaction condition: [MMA], 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}

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

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

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

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

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

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

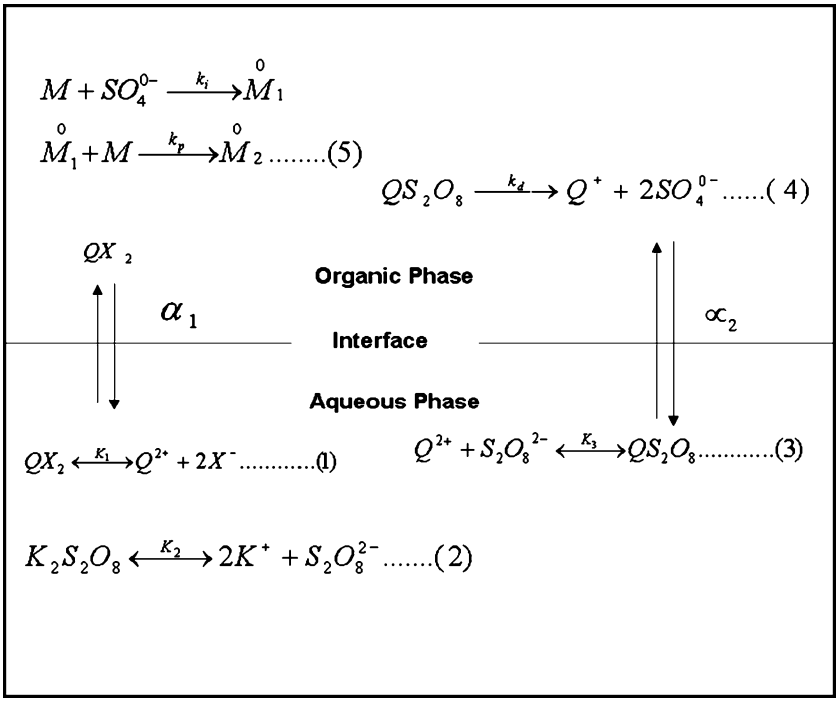
The growth of polymer chain according to the reaction in Eq. 5, the propagation step, is represented as follows:

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

Table 8 Effect of solvent polarity on Rp

Reaction conditions	Rp×10^5 mol dm^{-3} s^{-1}		
	Cyclohexanone (18.3)	Ethylacetate (3.91)	Cyclohexane (1.13)
[MMA]: 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 °C	2.28	1.56	1.090

Scheme 2 Polymerisation using multi-site phase transfer catalyst (MPTC) in an aqueous–organic two-phase system



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

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

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

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

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

$$2\overset{o}{M}_n \xrightarrow{K_t} \text{polymer} \tag{16}$$

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

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

Table 9 MMA-TBMABDC-$K_2S_2O_8$ system: degree of polymerisation

[MMA] mol dm^{-3}	$\bar{P}_n \times 10^{-3}$	$\frac{1}{P_n} \times 10^{-3}$
0.5	4.50	0.22
1.0	2.95	0.33
1.5	2.18	0.45
2.0	1.62	0.617
2.5	1.40	0.714
3.0	1.22	0.819

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

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

$$2K_d f K_3 \left[Q^{2+}\right]_w \left[S_2O_8^{2-}\right]_w = 2k_t \left[M^0\right]^2 \tag{19}$$

$$[\overset{0}{M}]^2 = \frac{K_d f K_3 [Q^{2+}]_w \left[S_2O_8^{2-}\right]_w}{k_t} \tag{20}$$

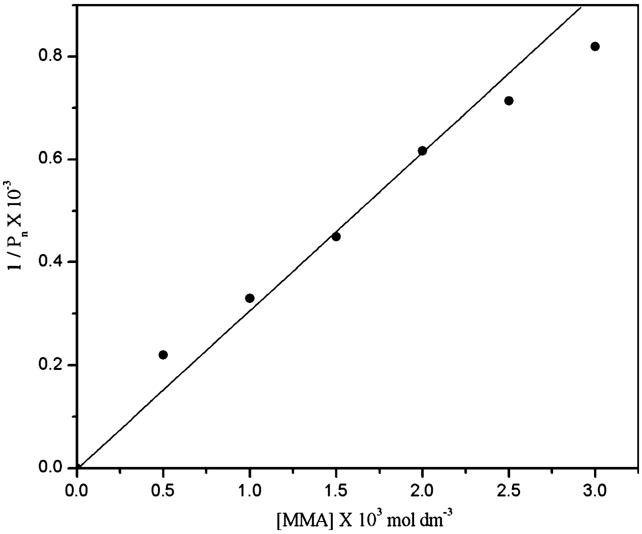


Fig. 7 MMA-MPTC-K2S2O8 system dependence of $\frac{1}{P_n}$ on [MMA]

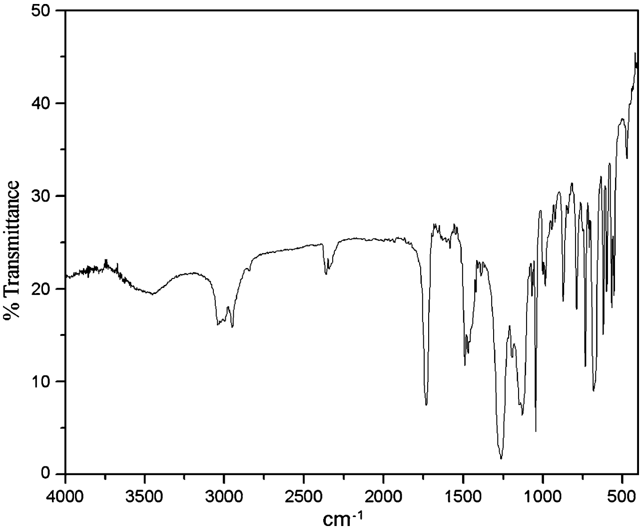


Fig. 8 FT-IR spectral analysis of poly (methyl methacrylate)

$$\overset{0}{[M]} = [\frac{K_d f K_3 [Q^{2+}]_w [S_2O_8^{2-}]_w}{k_t}]^{1/2} \tag{21}$$

Using Eqs. 15 and 21, the rate of polymerisation is represented as follows:

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

The above equation satisfactorily explains all the experimental observations. The expression for the degree of polymerisation is:

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

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

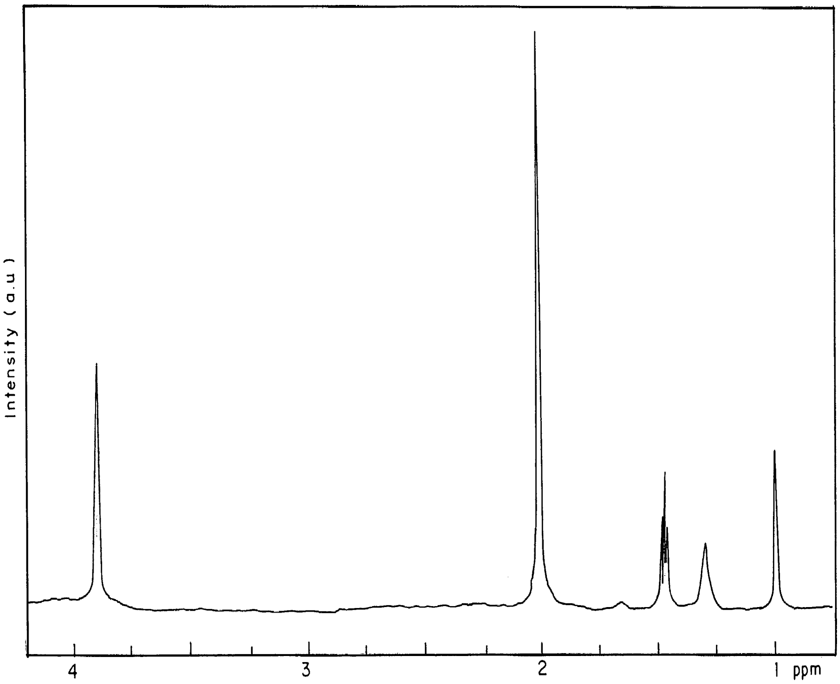
Equation 24 for the degree of polymerisation $\bar{P}_n$ is directionally proportional to $[M]^1$. It is found that a plot of $\bar{P}_n$ vs $[M]^1$ gives a straight line passing through the origin for MMA system (Table 9, Fig. 7). This observation supports the proposed mechanism.

Spectral analysis of poly(methyl methacrylate)

FT-IR spectroscopy

FT-IR spectra confirm a band of 1,732 cm^{-1} of ester stretching of atatic nature poly(methyl methacrylate) [18, 19]. The ester stretching bands in the region 1,100 to 1,300 cm^{-1} for isotactic and syndiotatic poly(methyl methacrylate) [20]. The following bands were observed in the spectra 1,128–1,262 cm^{-1} (C–O–C stretching band), 1,458 cm^{-1} (C–H deformation), 2,952 cm^{-1} (C–H stretching band) (Fig. 8).

Fig. 9 ^1H NMR spectral analysis of poly (methyl methacrylate)



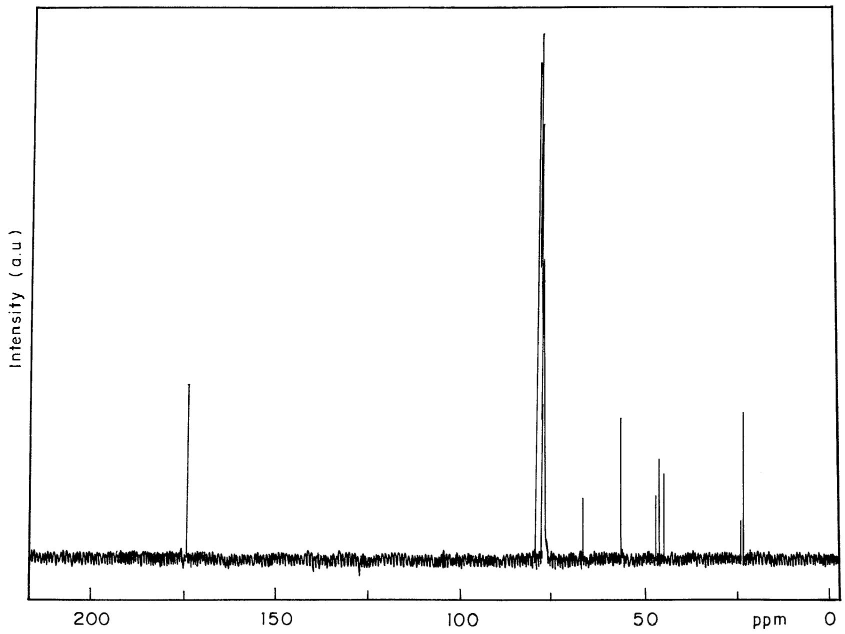


Fig. 10 *^{13}C* NMR spectral analysis of poly (methyl methacrylate)

^{1}H NMR spectral analysis

The *^{1}H* NMR spectrum (Fig. 9) shows the following peaks and confirms the structure of the polymer. The dominant signal of α-methyl proton in the range of 0.7–0.8 δ ppm corresponds to highly syndiotatic polymer [21], and the signal in the range of 0.9–1.0 δ ppm corresponds to the atatic and isotactic nature of the polymer. The α-methyl proton signals are assigned in the range of 0.9 to1.0 δ ppm, confirming the atatic nature of the polymer. The magnetic field experienced by ∝-methyl protons in syndiotatic, atatic and isotatic configuration may be expected to be different because of the strong magnetic anisotropy of the ester carbonyl group [22]. The signal in the 1.4 δ ppm range is assigned to the hydrogens in the polymer backbone. Signal at 3.8 δ ppm corresponds to the ester group.

^{13}C NMR spectral analysis

The *^{13}C* NMR spectra show a dominant peak at 45.2 δ ppm of the quaternary carbon group, confirming the atatic nature of the polymer [23]. The peaks at 44.9 and 45.8 δ ppm correspond to the syndiotatic and isotatic content of the polymer. The signals of carbonyl carbon (C=O), methylene carbon ($-CH_2$), methoxy carbon ($-OCH_3$) and methyl carbon ($-CH_3$) are placed in 171, 58, 52 and 22 δ ppm, respectively (Fig. 10).

Conclusions

The kinetics of the radical polymerisation of MMA was performed by using $K_2S_2O_8$ as initiator and TBMABDC as multi-site phase transfer catalyst in cyclohexane/water biphase system at 60±1 °C under nitrogen circumstances. The kinetic features, such as the rate of polymerisation (Rp), increase with increasing concentration of monomer, initiator and catalyst. The Rp increases with increasing temperature and solvent polarity. The orders with respect to monomer, initiator and catalyst were found to be 0.80, 1.0 and 0.5, respectively. Based on the results obtained, a suitable kinetic scheme and mechanism has been proposed. The polymer obtained by free-radical polymerisation of MMA was confirmed by spectral analysis.

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