

Multi-site phase transfer catalyzed radical polymerization of methyl methacrylate in mixed aqueous–organic medium: a kinetic study

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Abstract This work establishes the kinetics of radical polymerization of methyl methacrylate in an aqueous–organic two-phase system using 1,4-bis (triethylmethylammonium) benzene dichloride (TEMABDC) as multi-site phase transfer catalyst and potassium peroxydisulphate ($K_2S_2O_8$) as water-soluble initiator at 60 ± 1 °C under nitrogen atmosphere. The role of concentrations of monomer, initiator, catalyst, acid and ionic strength, temperature and volume fraction of aqueous phase on the rate of polymerization (R_p) was investigated. The rate of polymerization (R_p); $R_p \propto [MMA]^{0.64}$, $[TEMABDC]^{1.24}$ and $[K_2S_2O_8]^{1.50}$. The rate of polymerization increases with an increase in the concentration of monomer, initiator, catalyst and temperature. A generalized reaction model was developed to explain the phase transfer catalyzed polymerization reaction. Based on the kinetic results, radical mechanism has been derived. The activation energy and other thermodynamic parameters were calculated. The FT-IR spectroscopy validates a band of 1732 cm^{-1} of ester group of the obtained polymer. The viscosity average molecular weight of the PMMA was found 1.6955×10^4 g/mol.

Keywords Kinetics · Multi-site phase transfer catalyst · Radical polymerization · Rate of polymerization · Aqueous–organic media

Introduction

Phase transfer catalysis (PTC) is presently a well mature and established technique to accelerate the reactions between mutually insoluble two or more reactants located in different phases. In this technique, the two mutually insoluble reactants, one being an organic liquid or substrate dissolved in an organic solvent and other being an organic or inorganic salt from a solid or aqueous phase, react with the help of a phase transfer catalyst. It has been applied over 600 processes in variety of industries such as intermediates, dyestuffs, agrochemicals, perfumes, flavors, pharmaceuticals and polymers and value exceeds twelve billion (US\$) per year [1–4]. In polymer chemistry, they have been employed in synthesis of polymers [5–7], condensation polymerization [8], anionic polymerization [9, 10] and free radical polymerization [11–18].

In order to get the maximum desired product in a short duration of reaction period, the catalyst should be more efficient; with the aim of these requirements, novel “multi-site phase transfer catalysts” (multi-site PTC) have been developed which contain more than one catalytic active site per molecule. The concept of multi-sited phase transfer catalyst was introduced by Idoux et al. in which they have synthesized phosphonium and quaternary onium ions containing more than one active site per molecule [19]. The benefits of multi-site PTC are: enhance the rate of reaction with less time consumption and it transfers more number of active species from aqueous phase to organic phase during the reactions in contrast with single site—PTC. The reports on multi-site phase transfer catalyst aided radical polymerization of different alkyl methacrylates were gradually blooming in recent years [20–26]. The acrylic esters especially methyl methacrylate (MMA) are commercially fascinating and significant functional monomer for the

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synthesis of acrylic resins and various polymers based on poly(methyl methacrylate) (PMMA) with tunable properties. PMMA has good mechanical strength, acceptable chemical resistance and extremely good weather resistance. Further, it has favorable processing properties, good thermoforming and can be modified with pigments, flame retardant and UV absorbent additives [27, 28]. PMMA has vast profound and diverse applications that influence our lives every day. Radical polymerization is one of the best processes for the synthesis of polymers and the few important merits of radical polymerization are: it can be applied to all vinyl monomers under mild reaction condition with a wide range of temperature, it is water tolerant and its cost is relatively low. A curiosity on free radical polymerization has been stimulated to a great extent by the impressive progress made in several methods such as atom transfer radical polymerization (ATRP), nitroxyl radical-mediated polymerization (NMP), and reversible addition fragmentation transfer polymerization (RAFT). These methods and approaches were successfully introduced into polymerization process by different research groups [29–33]. Polymerization of MMA was effectively performed in ATRP [34, 35], NMP [36] and RAFT [37, 38]. The growth of a new kinetic model for the polymerization of methyl methacrylate (MMA) using novel catalyst and different methods at moderate temperature will be one of the major progresses in an industrial perspective.

The design, synthesis of novel catalysts and its applications in polymerization and organic reactions are a vital focus in the current research. Inspired by inherent characteristics of PTC technique and considering merits of water-soluble initiator, the present work endeavours to conduct a systematic investigation and explore the kinetics of free radical polymerization of methyl methacrylate (MMA) using potassium peroxydisulphate (PDS) as water-soluble initiator in the presence of synthesized multi-site phase transfer catalyst in cyclohexane/water two-phase system at 60 ± 1 °C. The role of various reaction variables on the rate of polymerization was studied, including the concentration of monomer, initiator, catalyst and temperature, aqueous phase variation. An extraction reaction model was proposed to explain the polymerization pathways and its significance was discussed.

Experimental

Chemicals and solvents

Methyl methacrylate (MMA, Sigma Aldrich, India) was first washed with 5% of aqueous sodium hydroxide to remove the inhibitor and washed with water to remove the

alkali and then dried over anhydrous calcium chloride at last distilled under reduced pressure. The middle fraction of the distillate was collected and stored in dark brown bottle at 5 °C in the refrigerator. The initiator, potassium peroxydisulphate ($K_2S_2O_8$, Merck, India), was purified twice by recrystallization in cold water. The solvents, cyclohexanone, cyclohexane, ethyl acetate, benzene and methanol (Avra, Merck, SRL, India) were used as received. The double distilled water was used to make an aqueous phase. The 1,4-bis (triethylmethylammonium) benzene dichloride (TEMABDC) was synthesized by adopting the reported procedure [39].

Synthesis of multi-sited phase transfer catalyst (TEMABDC)

Measured quantity of α - α' -dichloro-*p*-xylene (0.01 mol) was introduced into a 150 mL flask. Triethylamine (0.01 mol) in excess amount dissolving in ethanol (30 mL) was then introduced in the flask for the reaction with α - α' -dichloro-*p*-xylene under agitation speed 800 rpm at 60 °C for 24 h. Organic solvent ethanol and triethylamine were stripped in a vacuum evaporator. White precipitates of 1,4-bis (triethylmethylammonium) benzene dichloride (TEMABDC) were obtained. A white solid crystal of the product is obtained by recrystallizing the product in an ethanol solvent [39] (Scheme 1).

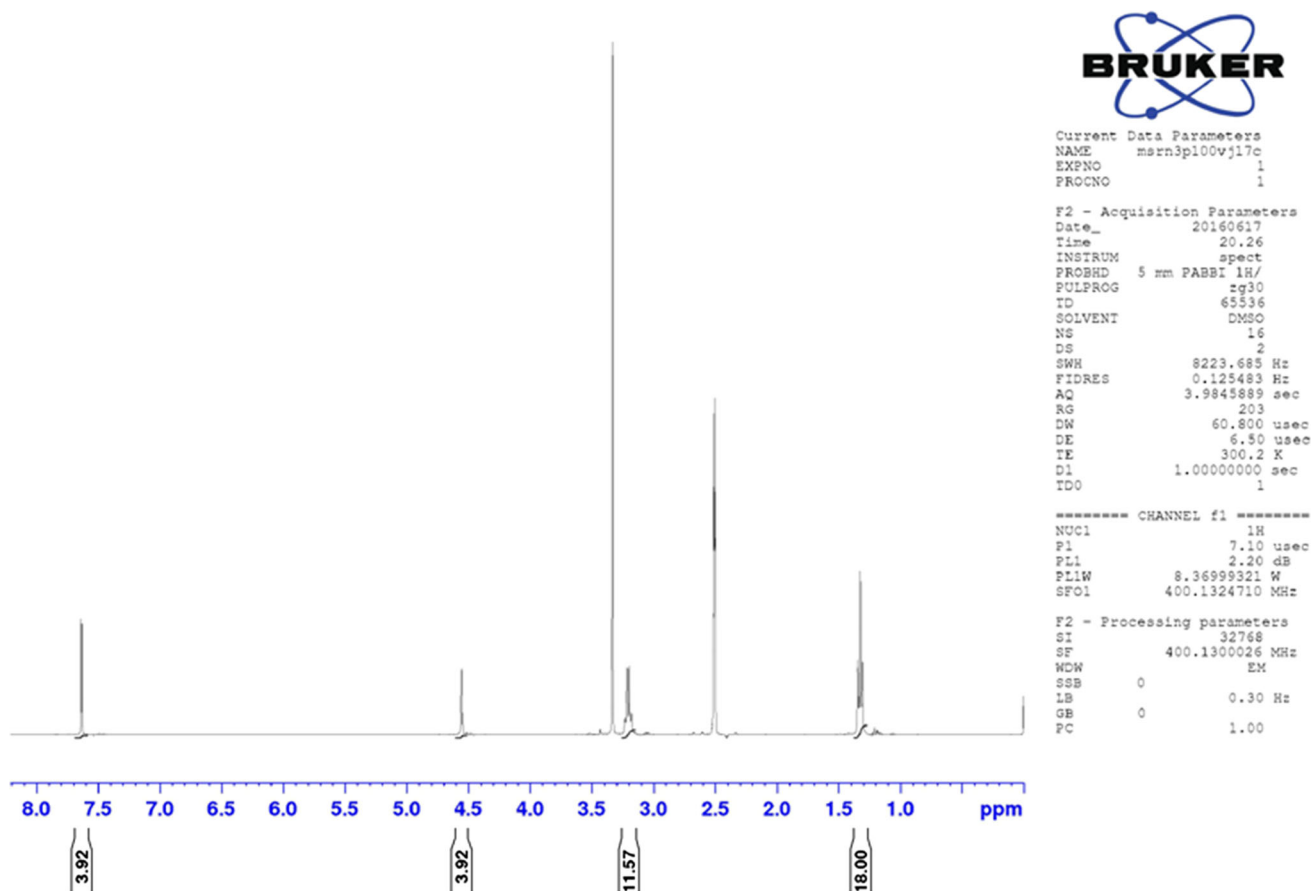
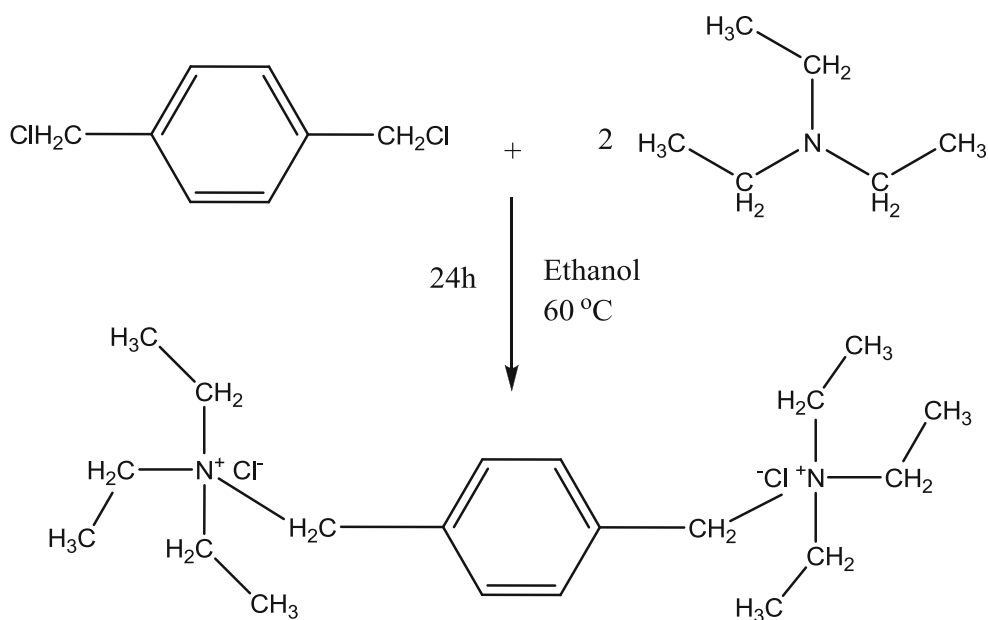
Characterization of multi-site PTC (TEMABDC):

^1H NMR analysis

^1H NMR spectra of 1,4-bis(triethylmethylammonium) benzene dichloride (TEMABDC) were recorded with BRUKER 400 MHz spectrometer using *d*-DMSO as a solvent and tetramethylsilane (TMS) as an internal reference. ^1H NMR: δ (400 MHz, *d*-DMSO): Benzyl, methylene and methyl protons are giving signals at 4.50, 3.0–3.50 and 1.30 ppm, respectively. The aromatic protons are well positioned at 7.6 ppm. An integrated total number of protons was good consistent with theoretical total protons of the catalyst (Fig. 1).

Polymerization of MMA

A polymerization experiment was carried out in annular glass ampoules with dimensions of 30 and 26 mm for outer and inner diameter, respectively, and 120 mm height. These ampoules have a surface area/volume ratio large enough for the heat transfer necessary to maintain the isothermal conditions during the polymerization. The total concentrations of 2.0 mol dm^{-3} of monomer (MMA) in the range of 4.5–9.5, 0.02 mol dm^{-3} of multi-site PTC (TEMABDC) from 1.5 to 2.5 mol dm^{-3} and the potassium

Scheme 1 Synthesis of multi-site phase transfer catalyst (TEMABDC)**Fig. 1** ^1H NMR analysis of 1,4-bis (triethylmethylammonium) benzene dichloride (TEMABDC)

peroxydisulphate (PDS) initiator varied from 1.5 to 2.5 mol dm^{-3} was used in the polymerization reaction. The ratio of monomer and catalyst was 1:0.01. The polymerization ampoule consists of equal volumes of aqueous

and organic phase (10 mL each). The monomer (MMA) in cyclohexane was the organic phase and the catalyst, sodium bisulfate (for adjusting the ionic strength $[\mu]$) and sulfuric acid (maintaining the $[\text{H}^+]$) were in the aqueous

phase. The ampoule was degassed using nitrogen gas continuously about 15 min after which it was sealed. Polymerizations were performed by placing the ampoules in a constant water bath at 60 ± 1 °C and the ampoules were removed from the water bath after a recorded time interval. The polymer was precipitated into large volume of ice cold methanol, filtered and dried at high vacuum until a constant weight was reached. The rate of polymerization (R_p) was calculated from the gravimetric determination of the polymer formed in a given time of polymerization. The R_p was calculated from the weight of polymer obtained using the formula:

$$R_p = 1000W/V \times t \times M,$$

where W is the weight of the polymer in gram; V is the volume of the reaction mixture in mL; t is the reaction time in seconds; M is the molecular weight of the monomer in g/mol. The kinetic experiment was carried out by changing the concentration of monomer, initiator, catalyst, temperature, etc., by adopting above stated polymerization procedure (Scheme 2). The average yield of polymer 65–70% was obtained in polymerization reaction on tuning of different reaction parameters.

Instruments

The FT-IR spectrum of poly (methyl methacrylate) was recorded on an FT-IR spectrometer (Perkin Elmer RX I) in the spectral region from 3500 to 500 cm^{-1} . A pellet of polymer sample was made with KBr on recording of spectrum. The 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 [40].

Reaction model

The rate of reaction involving two immiscible reactants is low due to less molecule collisions between them. To enhance the reaction rate, the common way to solve this difficulty is to carry out the reaction at extreme conditions or in a co-solvent. However, these efforts are generally

limited because a few side reactions occur at the extreme conditions or a desired co-solvent is not existent at all. Generally, this kind of situation in two-phase system, the rate of reaction dramatically enhanced with the help of phase transfer catalyst (PTC). PTC is capable of transferring the reactants of aqueous phase into organic phase, where the reaction will take place. In this aqueous–organic two-phase system, the reaction of QX (phase transfer catalyst) and KY (initiator) in the aqueous phase produces QY at the interface between the two phases where it was decomposed and produced the radical ions which initiate the polymerization reactions at 60 ± 1 °C. The simple representation of this process is shown in Scheme 3.

Results and discussion

The radical polymerization of methyl methacrylate initiated by multi-site PTC- $\text{K}_2\text{S}_2\text{O}_8$ in cyclohexane-water two-phase systems was examined at 60 ± 1 °C with changing various reaction parameters, which influence the rate of polymerization.

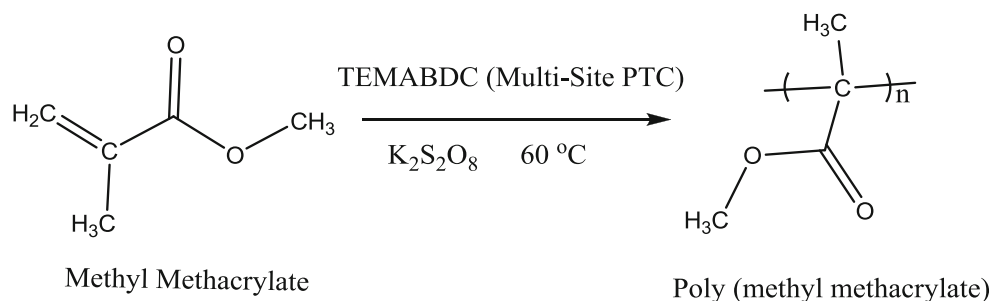
Steady state rate of polymerization

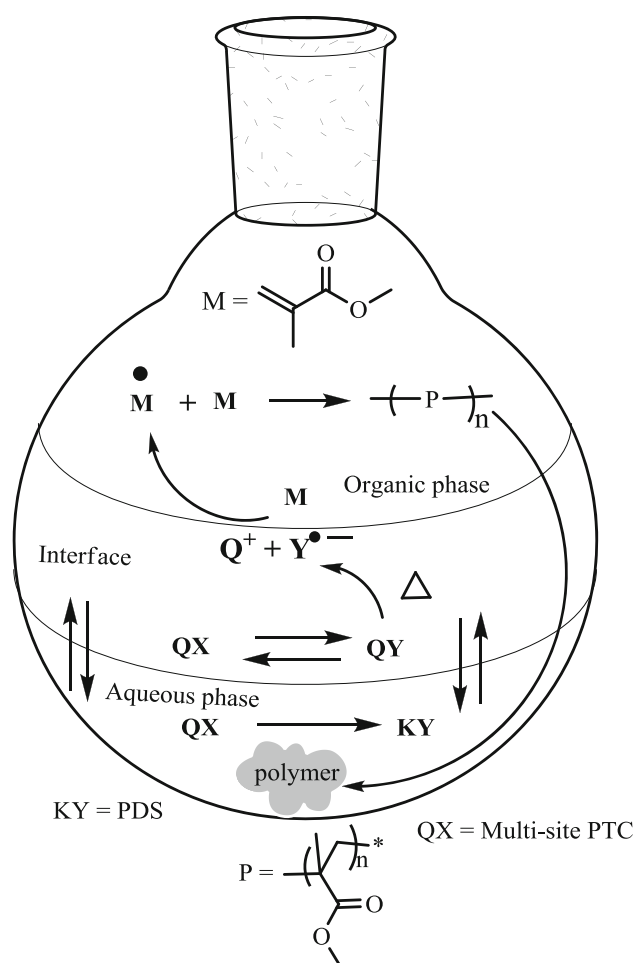
The steady-state rate of polymerization for the methyl methacrylate was studied first by carrying out the experiments at regular intervals of time with fixed concentrations of all other parameters. The rate of polymerization (R_p) increases nicely to some extent, slightly decreases thereafter and reaches constant value [21]. The plot of R_p versus time shows that the steady-state rate of polymerization of MMA was obtained at 40 min. Hence, the polymerization reaction time was fixed at 40 min to carry out the experiments with changing various reaction parameters (Fig. 2).

Role of [MMA] on the rate of polymerization (R_p)

The role of [MMA] on the rate of polymerization (R_p) was studied by changing the concentrations in the range of 4.5–9.5 mol dm^{-3} by keeping the concentrations of

Scheme 2 Polymerization of methyl methacrylate (MMA) in two-phase system





Scheme 3 Reaction model for polymerization of MMA in an aqueous–organic media

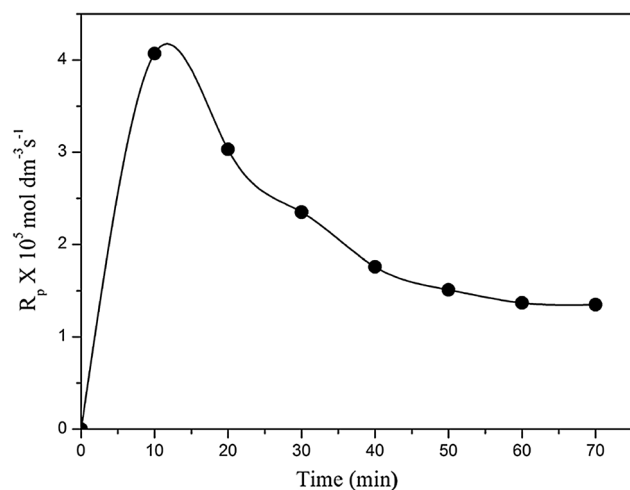


Fig. 2 Steady-state rate of polymerization. Reaction condition: [MMA]: 2.0 mol dm^{-3} ; $[\text{K}_2\text{S}_2\text{O}_8]$: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; [TEMABDC]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+]$: 0.50 mol dm^{-3} ; $[\mu]$: 0.20 mol dm^{-3} ; temperature: $60 \pm 1 \text{ }^\circ\text{C}$

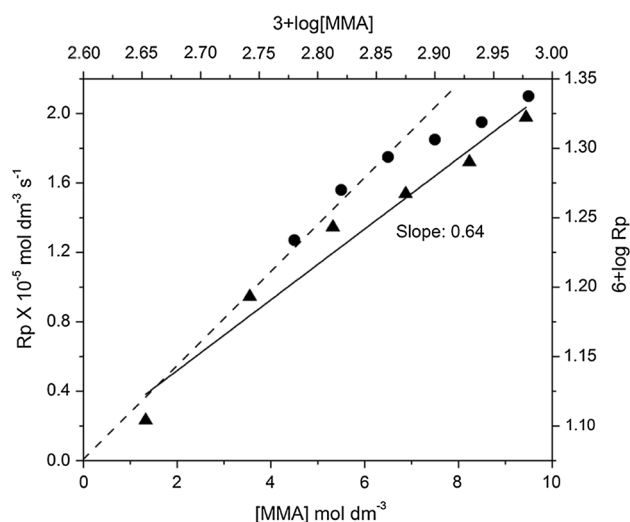


Fig. 3 Role of [MMA] on the R_p . Reaction condition: $[\text{K}_2\text{S}_2\text{O}_8]$: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; [TEMABDC]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+]$: 0.50 mol dm^{-3} ; $[\mu]$: 0.20 mol dm^{-3} ; Temperature: $60 \pm 1 \text{ }^\circ\text{C}$; Time: 40 min

potassium peroxydisulphate (initiator), multi-site phase transfer catalyst, ionic strength and pH constant. The R_p increases with increase in the concentration of the monomer. The reaction orders with respect to monomer concentration were determined from the slope of $6 + \log R_p$ versus $3 + \log [\text{MMA}]$ and the reaction order with respect to the monomer concentration was found to be 0.65. The plot of R_p versus [MMA] passing through the origin confirms the above observations with respect to [MMA] (Fig. 3). The half-order with respect to concentration of monomer has been reported for the polymerization of *n*-butyl methacrylate and ethyl methacrylate with other multi-site PTC using potassium peroxydisulphate as initiator [23–25].

Role of $[\text{K}_2\text{S}_2\text{O}_8]$ on the rate of polymerization (R_p)

The role of $[\text{K}_2\text{S}_2\text{O}_8]$ on the rate of polymerization was studied by varying its concentration in the range of $1.5\text{--}2.5 \text{ mol dm}^{-3}$ at fixed concentrations of other parameters. The R_p increases with increasing concentration of initiator for MMA system. The initiator order value was calculated from the plot of $6 + \log R_p$ versus $3 + \log [\text{K}_2\text{S}_2\text{O}_8]$ the slope was found to be 1.50. As expected a plot of R_p versus $[\text{K}_2\text{S}_2\text{O}_8]$ is linear passing through the origin supporting the above deduction (Fig. 4). Generally, the rate of polymerization is proportional to the square root of initiator concentration at a condition that the termination is bimolecular. In case, if the termination takes place by combination of primary radicals, the initiator order is expected to deviate from half order. However, in this study,

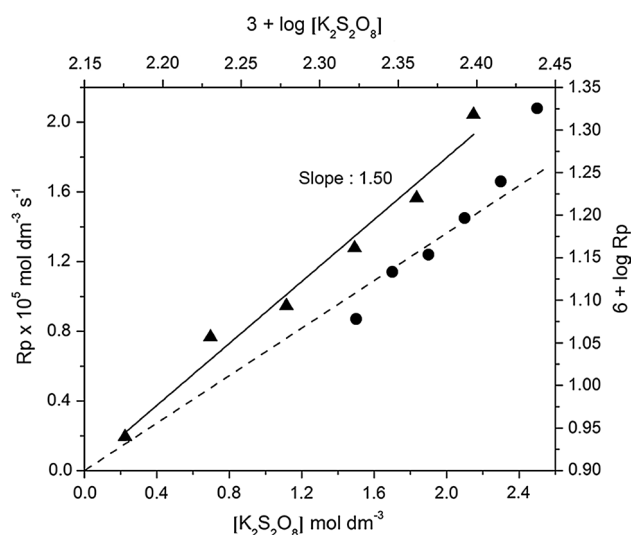


Fig. 4 Role of $[K_2S_2O_8]$ on the R_p . Reaction condition: $[MMA]$: 2.0 mol dm^{-3} ; $[TEMABDC]$: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[H^+]$: 0.50 mol dm^{-3} ; $[\mu]$: 0.20 mol dm^{-3} ; temperature: $60 \pm 1 \text{ }^\circ\text{C}$; time: 40 min

the initiator order was found to be greater than half and it may be attributed to gel effect or diffusion-controlled termination constant [41].

Role of [TEMABDC] on the rate of polymerization (R_p)

The role of concentration of 1,4-bis (triethylmethylammonium) benzene dichloride (TEMABDC) on the rate of polymerization was studied by varying its concentration in the range from 1.5 to 2.5 mol dm^{-3} at fixed concentrations of other parameters. From the slope of linear plot obtained by plotting of $6 + \log R_p$ versus $3 + \log [TEMABDC]$, the order with respect to [TEMABDC] was found to be 1.24. The observed order was confirmed from the straight line passing through the origin in a plot of R_p versus [TEMABDC] (Fig. 5). An increase in the rate of polymerization with an increase in the concentration of catalyst may attribute to the number of active site (multi-site) of catalyst, thus giving an opportunity to collision between initiator and catalyst. Thereby, more reactive intermediates enhance the rate of polymerization [42].

Blank experiment: polymerization of methyl methacrylate was carried out by adopting mentioned polymerization procedure without adding catalyst at $60 \pm 1 \text{ }^\circ\text{C}$ for 40 min. The changes in the appearance of two-phase media were observed (slight turbid), but while pouring the reaction mixture into methanol it was disappeared. This observation was the proof for role of catalyst on the polymerization reaction. The polymerization did not occur in the absence of catalyst even after several mints.

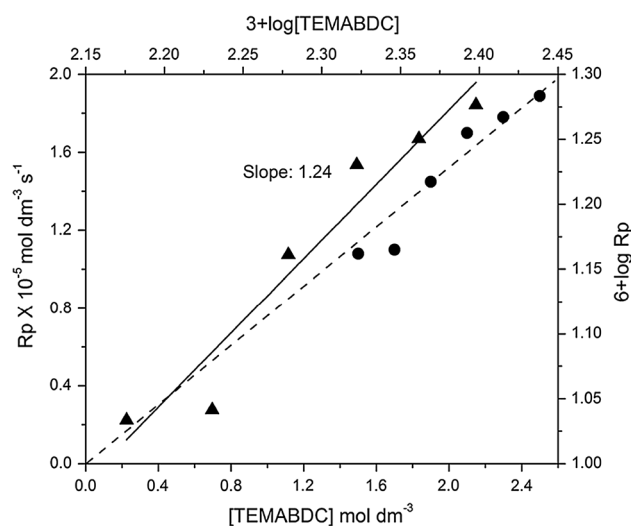


Fig. 5 Role of [TEMABDC] on the R_p . Reaction condition: $[MMA]$: 2.0 mol dm^{-3} ; $[K_2S_2O_8]$: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[H^+]$: 0.50 mol dm^{-3} ; $[\mu]$: 0.20 mol dm^{-3} ; Temperature: $60 \pm 1 \text{ }^\circ\text{C}$; Time: 40 min

Role of temperature on the R_p

The role of variation of temperature 50–65 $^\circ\text{C}$ on the rate of polymerization was investigated by keeping other parameters constant. The rate of polymerization increases with an increase in temperature. This may be due to the fact that when the temperature is gradually raising the rate of initiator decomposition was also increased drastically and thus yields more radicals which are responsible to accelerate the polymerization process promptly thereby the rate of polymerization was increased significantly. The overall activation energy of polymerization (E_a) was found to be 18.51 k J/mol (Table 1; Fig. 6). The higher E_a value of 66.36 kJ/mol was reported for the phase transfer catalyzed radical polymerization of *n*-butyl acrylate in two-phase systems. From the E_a value, we believe that multi-site PTC polymerization occurs promptly than reported [43]. The thermodynamic parameters such as entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger) and free energy of activation (ΔG^\ddagger) have been calculated and presented in Table 2.

Role of acid $[H^+]$ on R_p

The role of different concentrations of acid in the range 0.16–0.24 mol dm^{-3} on the rate of polymerization reaction was examined at fixed concentrations MMA, PDS, TEMABDC and at constant ionic strength. R_p was found to be almost independent of variation of acid strength in the range employed in this experiment (Table 3). A similar kind of observation was reported on phase transfer catalyzed polymerization reactions [20–23].

Table 1 Role of temperature on the rate of polymerization

Temperature, K	$R_p \times 10^5 \text{ mol dm}^{-3} \text{ s}^{-1}$	$1/T \times 10^{-3} \text{ K}^{-1}$	$6 + \log [R_p]$
323	1.2970	3.0959	1.1129
328	1.3801	3.0487	1.1399
333	1.4470	3.0030	1.1936
338	1.7460	2.9585	1.2420

Reaction condition: [MMA]: 2.0 mol dm^{-3} ; $[\text{K}_2\text{S}_2\text{O}_8]$: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; [TEMABDC]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+]$: 0.50 mol dm^{-3} ; $[\mu]$: 0.20 mol dm^{-3}

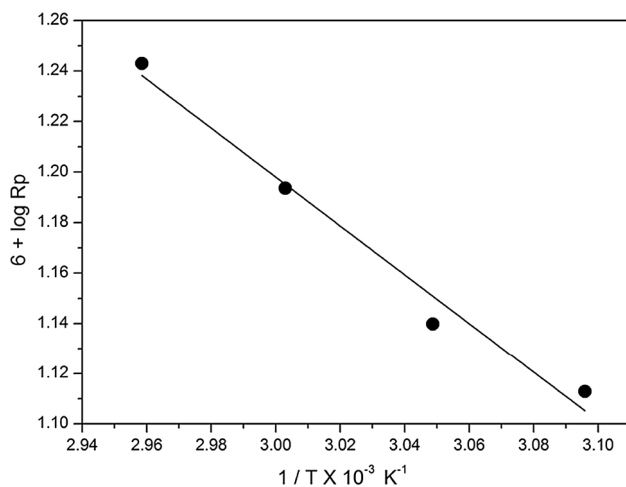


Fig. 6 Role of temperature on the R_p . Reaction condition: [MMA]: 2.0 mol dm^{-3} ; $[\text{K}_2\text{S}_2\text{O}_8]$: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; [TEMABDC]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+]$: 0.50 mol dm^{-3} ; $[\mu]$: 0.20 mol dm^{-3} ; time: 40 min

Table 2 Thermodynamic parameters

E_a k J/mol	ΔG^\ddagger k J/mol	ΔH^\ddagger k J/mol	ΔS^\ddagger eu
18.51	53.29	14.33	-117.00

Table 3 Role of $[\text{H}^+]$ on the rate of polymerization

$[\text{H}^+] \text{ mol dm}^{-3}$	$R_p \times 10^5 \text{ mol dm}^{-3} \text{ s}^{-1}$
0.16	1.3590
0.18	1.3731
0.20	1.3940
0.22	1.4238
0.24	1.4312

Reaction condition: [MMA]: 2.0 mol dm^{-3} ; $[\text{K}_2\text{S}_2\text{O}_8]$: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; [TEMABDC]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\mu]$: 0.60 mol dm^{-3} ; Temperature: $60 \pm 1 \text{ }^\circ\text{C}$

Role of ionic strength (μ) on the R_p

To find out the role of ionic strength on the R_p , the ionic strength of the reaction medium was varied from 0.50 to 0.70 mol dm^{-3} by keeping other reaction parameters are

Table 4 Role of $[\mu]$ on the rate of polymerization

$[\mu] \text{ mol dm}^{-3}$	$R_p \times 10^5 \text{ mol dm}^{-3} \text{ s}^{-1}$
0.50	1.6023
0.55	1.5826
0.60	1.5982
0.65	1.6145
0.70	1.6210

Reaction condition: [MMA]: 2.0 mol dm^{-3} ; $[\text{K}_2\text{S}_2\text{O}_8]$: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; [TEMABDC]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{H}^+]$: 0.20 mol dm^{-3} ; Temperature: $60 \pm 1 \text{ }^\circ\text{C}$

constant. The results show that the R_p was not much influenced on the variation of concentrations of ionic strength of the medium in this investigation (Table 4). An independent nature of ionic strength on the rate of polymerization in the phase transfer catalyzed polymerization was reported [20–23].

Role of organic solvents polarity on R_p

The role of organic solvents polarity on the R_p was examined by carrying out the polymerization in three solvents cyclohexane, ethylacetate and cyclohexanone having the dielectric constants 2.02, 6.02 and 18.03, respectively. It was found that the R_p decreased in the following order: cyclohexanone > ethyl acetate > cyclohexane. An increase in the rate of polymerization was attributed to the increase in the polarity of the solvents, which facilitates greater transfer of peroxydisulfate ion from aqueous phase to organic phase [20–26, 42] (Table 5).

Role of variation of aqueous phase on R_p

Polymerization reactions were conducted with a constant volume of organic phase and changing the volumes of aqueous phase ($V_w/V_o = 0.29\text{--}0.90$) at fixed concentrations of all other parameters. The variation of aqueous phase was found to exert no significant change in the rate of polymerization. It has been reported that the variation of aqueous phase on R_p was not affected significantly on phase transfer catalyzed polymerization studies [24–26].



Table 5 Role of organic solvent polarity on the rate of polymerization

Experimental conditions	$R_p \times 10^5 \text{ mol dm}^{-3} \text{ s}^{-1}$		
	Cyclohexanone (18.3)	Ethylacetate (3.91)	Cyclohexane (1.13)
[MMA]: 2.0 mol dm^{-3}	2.15	1.52	1.06
[$\text{K}_2\text{S}_2\text{O}_8$]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$			
[TEMABDC]: $2.0 \times 10^{-2} \text{ mol dm}^{-3}$			
[H^+]: 0.50 mol dm^{-3}			
[μ]: 0.20 mol dm^{-3}			
Temperature: $60 \pm 1 \text{ }^\circ\text{C}$			

Mechanism and rate law

Scheme 4 represents the reactions characterizing the polymerization of methyl methacrylate (M) initiated by $\text{K}_2\text{S}_2\text{O}_8/\text{MPTC}$ in cyclohexane/water two-phase systems. It is assumed that dissociation of QX and $\text{K}_2\text{S}_2\text{O}_8$, formation of QS_2O_8 in aqueous phase, and initiation of monomer in organic phase occur 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 (α_1 and α_2) of QX and QS_2O_8 are defined as follows, respectively.

$$K_1 = \frac{[\text{Q}^{2+}]_w [\text{X}^-]_w^2}{[\text{QX}]_w} \quad (6)$$

$$K_2 = \frac{[\text{K}^+]_w^2 [\text{S}_2\text{O}_8^{2-}]_w}{[\text{K}_2\text{S}_2\text{O}_8]_w} \quad (7)$$

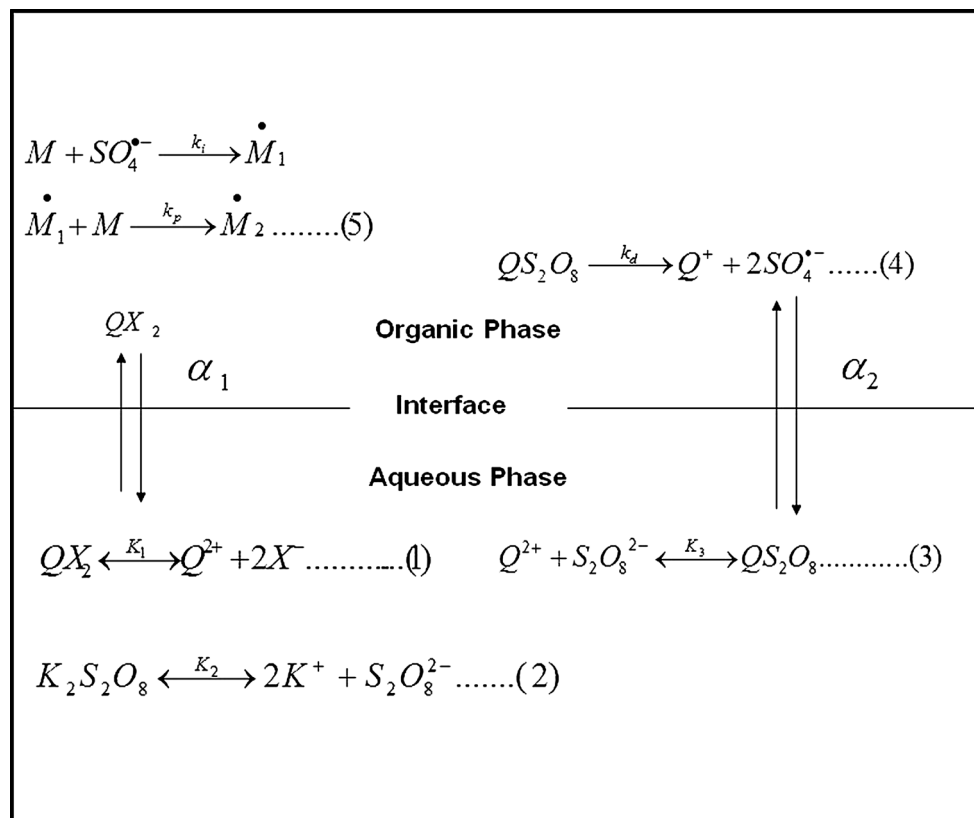
$$K_3 = \frac{[\text{QS}_2\text{O}_8]_w}{[\text{Q}^+]_w [\text{S}_2\text{O}_8^{2-}]_w} \quad (8)$$

$$\alpha_1 = \frac{[\text{Q}^{2+}\text{X}_2^-]_w}{[\text{QX}]_o} \quad (9)$$

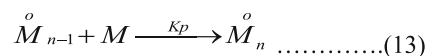
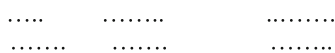
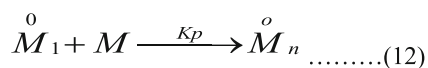
$$\alpha_2 = \frac{[\text{Q}^{2+}\text{S}_2\text{O}_8^{2-}]_w}{[\text{QS}_2\text{O}_8]_o} \quad (10)$$

The initiation rate (R_i) of radical, $\text{SO}_4^{\cdot-}$ in Eq. (4), may be represented as follows; f is the initiator efficiency:

$$R_i = \frac{d[\text{SO}_4^{\cdot-}]}{dt} = 2K_d f K_3 [\text{Q}^+]_w [\text{S}_2\text{O}_8^{2-}]_w \quad (11)$$

Scheme 4 Polymerization pathways of MMA-TEMABDC-PDS in an aqueous–organic medium

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



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

$$R_p = k_p [\overset{\circ}{M}] [M] \quad (14)$$

$$[\overset{\circ}{M}] = \frac{R_p}{k_p [M]} \quad (15)$$

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



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

$$R_t = 2k_t [\overset{\circ}{M}]^2 \quad (17)$$

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

$$R_i = R_t \quad (18)$$

$$2K_d f K_3 [Q^+]_w [S_2O_8^{2-}]_w = 2k_t [\overset{\circ}{M}]^2 \quad (19)$$

$$[\overset{\circ}{M}]^2 = \frac{K_d f K_3 [Q^+]_w [S_2O_8^{2-}]_w}{k_t} \quad (20)$$

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

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

$$R_p = k_p \left[\frac{k_d K_3 f}{k_t} \right]^{1/2} [Q^{2+}]_w^{1.2} [S_2O_8^{2-}]_w^{1.50} [M]^{0.64} \quad (22)$$

The above equation satisfactorily explains all the experimental observations for multi-site phase transfer catalyzed radical polymerization of methyl methacrylate in an aqueous–organic two-phase system.

Determination of viscosity average molecular weight of polymer

The viscosity average molecular weight (M_v) of the PMMA was determined using the intrinsic and reduced viscosity of the polymer solution obtained from the viscosity measurement. Viscosity measurements were performed in an Ubbelohde viscometer. The principle behind capillary viscometry is the Poiseuille's law, which states that the time of flow of a polymer solution through a thin capillary is proportional to the viscosity of the solution. The flow time of the pure solvent and different concentration of the polymer solution was measured (Table 6). The few important and well-established terms related to viscosity of polymer solutions are defined as: Relative viscosity, $\eta_r = \eta/\eta_o$ (flow time of polymer solution/flow time of pure solvent); Specific viscosity, $\eta_{sp} = \eta_r - 1$; Reduced viscosity, $\eta_{red} = \eta_{sp}/C$; The intrinsic viscosity of the polymer is related to its molecular weight related by Mark–Houwink equation. $[\eta] = KM_v^a$ where 'K' and 'a' are constants for a polymer, solvent and at a temperature ($K = 5.2 \times 10^{-5}$; $a = 0.760$ for benzene at 30 ± 1 °C); M_v represents the viscosity average molecular weight of the polymer. The viscosity average molecular weight of the PMMA was found to be 1.6955×10^4 g/mol (Fig. 7).

Characterization of polymer: FT-IR analysis

The FT-IR spectra of PMMA with sharp band of ester stretching frequency at 1720 cm^{-1} confirm the atactic nature of PMMA [44]. The conformational assignment of the ester band was in the region of $1100\text{--}1300 \text{ cm}^{-1}$ for isotactic and syndiotactic PMMA [45, 46]. The following bands were observed in the spectra 1124 cm^{-1} (C–O–C stretching band), 1458 cm^{-1} (C–H deformation), and 2924 cm^{-1} (C–H stretching band) (Fig. 8).

Table 6 Determination of viscosity average molecular weight (M_v) of PMMA

Concentration (C, g/mL)	Flow time (s) t_1 t_2	Average	$\eta_r = t/t_o$	$\ln \eta_r$	$\ln \eta_r/C$	η_{sp}/C
Benzene (solvent)	45.02 45.26	45.14 (t_o)				
0.02	47.00 47.01	47.00	1.0142	0.0403	2.0189	0.0412
0.04	48.78 48.72	48.75	1.0799	0.0769	1.9234	0.0799
0.06	49.34 49.09	49.21	1.0901	0.0863	1.4388	0.0901
0.08	50.15 50.18	50.16	1.1112	0.1054	1.3181	0.1112
0.10	51.12 51.16	51.14	1.1329	0.1247	1.2479	0.1329

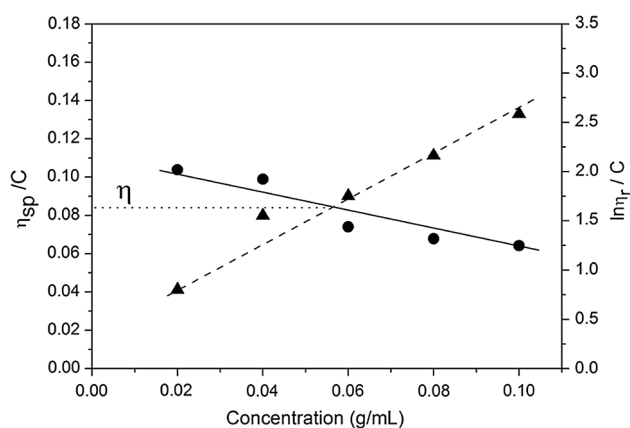


Fig. 7 Determination of viscosity average molecular weight of PMMA

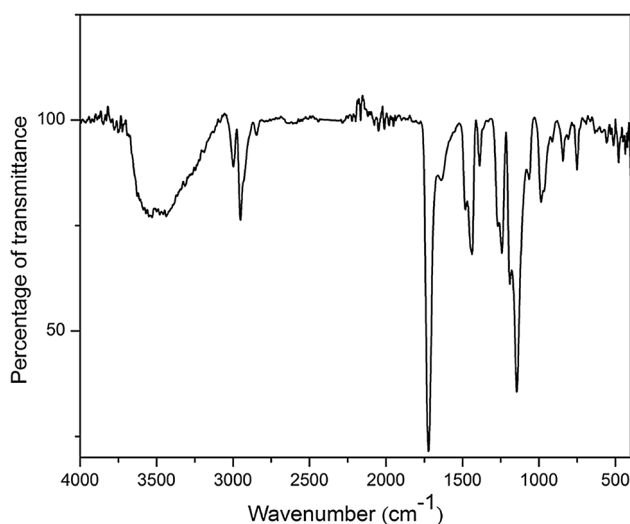


Fig. 8 FT-IR spectral analysis of poly(methyl methacrylate)

Conclusions

Free radical polymerization of methyl methacrylate was successfully performed with the help of 1,4-bis (triethyl methyl ammonium) benzene dichloride (TEMABDC) as multi-site phase transfer catalyst and potassium peroxydisulphate as initiator in two-phase system. The kinetic features, such as the rate of polymerization (R_p), increase with increasing concentration of [MMA], [$K_2S_2O_8$], [TEMABDC] and temperature. An absence of multi-site PTC polymerization did not occur; it reveals that the catalyst was responsible for polymerization reaction. The aqueous phase, acid and ionic strength of the medium do not show any appreciable effect on the R_p . The phase transfer catalyzed polymerization of methyl methacrylate follows a half order with respect to monomer, one and half-order with respect to initiator and order of unity for

catalyst. Based on the results obtained, a suitable mechanism has been proposed. The polymer obtained through radical polymerization of methyl methacrylate was confirmed by FT-IR analysis. The viscosity average molecular weight of the PMMA was found to be 1.6955×10^4 g/mol. Multi-site PTC accelerates the polymerization reaction promptly in two-phase system using water-soluble initiator. The development of feasible pathways for the synthesis of polymers is an important goal in processing industries. Hence, this methodology could be a great interest in synthesis of polymers or any industrially important compounds where the immiscible reactants located in different phase.

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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest regarding the publication of this article.

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