

## Free radical polymerization of methyl methacrylate under the influence of ultrasound assisted a new bisite phase-transfer catalyst system- A kinetic study

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### Abstract

The kinetics of multi-site phase-transfer catalyzed free radical polymerization of methyl methacrylate (MMA) using potassium peroxy disulphate (PDS) as water soluble initiator and newly synthesized 1,4-dihexadecylpyrazine-1,4-dium dibromide as multi-site phase-transfer catalyst (MPTC) has been investigated in ethyl acetate / water two phase system at constant temperature  $50 \pm 1^\circ\text{C}$  under nitrogen atmosphere and ultrasound irradiation conditions. The rate of polymerization increases with an increase in concentrations of MMA, PDS and MPTC. The order with respect to monomer, initiator and MPTC were found to be 1.0, 0.5 and 0.5 respectively. Based on the observed results a suitable mechanism has been proposed to account for the experimental observations and its significance was discussed.

*Key words :* Multi-site phase-transfer catalyst; radical polymerization; methyl methacrylate, Ultrasound; Kinetic study.

### 1. Introduction

The reaction between mutually immiscible reactants were usually difficult to conduct efficiently even under severe operating. Such problems as low reaction rate, low

conversion of reactants and low formation of products can be over come by phase-transfer catalysis technique (PTC). The phase-transfer catalysts usually as quaternary onium salts, crown ethers, cryptands etc., can be applied to give a high conversion and products selectivity.

Phase-transfer catalysis is considered to be one of the most efficient tools in all branches of chemistry because of its simplicity, high conversion, under very mild reaction condition and environmental concern. It is widely used for manufacturing pharmaceuticals, agricultural chemicals, perfumes, flavours, dyes, polymers and environmental applications<sup>1-3</sup>. The phase-transfer catalyzed free-radical polymerization of vinyl monomers with water-soluble initiators like potassium peroxydisulphate (PDS) and ammonium peroxydisulphate (ADS) is a relatively new area of research<sup>4</sup>. It has been found that such water soluble initiators have been used effectively for bulk or solution polymerization with phase-transfer catalysts<sup>5,6</sup>. Many authors reported the single-site PTC assisted radical polymerization of hydrophobic vinylic monomers in aqueous-organic two phase system<sup>7,8</sup>. Recently, the catalytic behaviour of multi-site phase-transfer catalysts have been attracted much attention, due to the fact that multiple molecules of the aqueous reactant can be carried into the reaction phase once a reaction cycle. The catalytic efficiency is thus enhanced<sup>9,10</sup>. The first report published on multi-site PTC (MPTC) was by Idoux *et al.*, and they have synthesized phosphonium and quaternary onium ions containing more than one site per molecule<sup>11</sup>. Vajjiravel *et al.*<sup>12</sup> reported the kinetics of free radical polymerization of acrylonitrile using multi-site PTC-PDS system in organic-water biphasic medium.

The application of ultrasound irradiation in organic synthesis has been broadly extended in recent years. It enhances the reaction rate and selectivity of the product rather significantly. Many studies have been carried out and it is well documented that the advantages of

ultrasound procedures are good yields, short reaction times and mild conditions<sup>13-16</sup>. Ultrasound irradiation method is now recognized as a viable environmentally benign alternatives<sup>17-22</sup>. Recently reported studies reveals that ultrasound technique combined with PTC are proved to be an useful technique in heterogeneous organic<sup>23-29</sup> and polymerization reactions<sup>30-35</sup>. However the combinations of water soluble multi-site PTC with ultrasonic irradiation for free radical polymerization of vinyl monomers have not been reported. In this study we reporting the synthesis of a new multi-site phase-transfer catalyst viz., 1,4-dihexadecylpyrazine-1,4-diium dibromide which is used for the free radical polymerization of ethyl methacrylate using potassium peroxydisulphate (PDS) as water soluble initiator in ethyl acetate/water biphasic media at  $55 \pm 1^\circ\text{C}$  in association with ultrasound wave energy (28 kHz, 300 W).

## 2. Experimental

### 2.1 Chemicals and equipments :

Pyrazine (Aldrich – USA), MMA (Aldrich – USA) was washed with 2% NaOH solution to remove inhibitor (HCl) and again washed with double distilled water to remove the basic impurities. All other reagents Potassium peroxydisulphate (PDS) (Merck, Mumbai, India), n-cetyl bromide (Aldrich, Mumbai) and methanol (SRL) were used as received without further purification.

The FT-IR spectra were recorded on a Bruker-Tensor 27 FT-IR spectrophotometer. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker 400 MHz and 100 MHz spectrometer using TMS as an internal standard

and  $\text{CDCl}_3$  as the solvent. Elemental analysis was performed on a Perkin-Elmer 240B elemental analyzer.

## 2.2 Ultrasonic process equipment :

Ultrasonic energy is transmitted to the process vessel through the liquid medium, usually water in the tank. For safety purpose, the sonochemical reactor consisted of two layers stainless steel body. The sonochemical reactor configuration used in the present work is basically an ultrasonic bath with liquid holding capacity of 5 litres. The reactor has an operating frequency of 28 kHz and 40 kHz with a output of 300W. Both ultrasounds are separately produced through flat transducer mounted at the bottom of the tank. In this ultrasonic instrument there is a provision for a drain as well as an outlet at the top, which gives facility of continuous operation of work. The process vessel is immersed in the water present in the tank. An additional heater with a facility of temperature controller has also been provided so as to facilitate some high and low temperature reactions. If the water level is lower than the outlet *i.e.*, 3 cm below from the top of the sonicator, the applied frequency is automatically cut off. So the water fill is important. The reactor was made of Pyrex glass polymer tube fitted with an inlet and outlet for nitrogen. An inert atmosphere was maintained inside the reaction tubes by closing the inlet and outlet with rubber gaskets. This reaction vessel was supported at the center of the ultrasonic cleaning bath 2 cm above from the position of the transducer which is fixed at the bottom of the ultrasonicator to get the maximum ultrasonic energy. All the experimental parameters were done at 28 kHz with output power of 300 W.

## 2.2 Ultrasonic power measurement by calorimetry :

Experiments were carried out to evaluate the actual ultrasound intensity absorbed by the liquid by calorimetry. The ultrasonic energy dissipated in the liquid can be determined by the following equation<sup>36</sup>

$$P = Mc_p (dT/dt)$$

Thus

$$T - T_0 = P / (Mc_p) t$$

Where P is the power (J/min), M is the mass of the water (g),  $c_p$  is the specific heat of water ( $\text{J g}^{-1} \text{K}^{-1}$ ),  $dT/dt$  is the rate of temperature rise ( $\text{K min}^{-1}$ ),  $T_0$  is the initial temperature and T is the temperature as a function of time. Eq. (2) assumes that the liquid is pure and there is no heat loss from the system. The experiment was conducted with the same beaker used for polymer degradation experiments with the same amount of liquid. The experiments were conducted for 15 min and the increase of temperature of the liquid was monitored as a function of time. This was plotted and linearly regressed based on Eq. (2) to obtain the power supplied. The experiments were conducted with both chlorobenzene and water and all experiments were repeated thrice to check the consistency of the results. Because the value of  $c_p$  is different for chlorobenzene and water, the rise in temperature of the liquid was different but the value of the power obtained was the same in both the cases.

## 2.3 Determination of Molecular Weight of Polymer :

The viscosity average molecular weight

of the polymer was determined using the intrinsic viscosity of the polymer solution obtained from viscosity measurement and appropriate Mark-Houwink equation<sup>37</sup>.

Viscosity measurements were made in an Ubbelohde suspended level dilution viscometer equipped with a large reservoir permitting dilutions to be made in the viscometer itself. Flow times for solutions of different concentrations were measured and compared with that of the pure solvent.

The relative viscosity ( $\eta_r$ ) of the polymer solution was calculated from the equation

$$\eta_r = \eta / \eta_o = \frac{\text{Flow time for polymer solution}}{\text{Flow time for pure solvent}}$$

$\eta$  – viscosity of polymer solution

$\eta_o$  – viscosity of pure solvent

The relative increase in the viscosity called specific viscosity ( $\eta_{sp}$ ) is given by

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} = \frac{\eta}{\eta_o} - 1 = \eta_r - 1$$

The relative increase in specific viscosity per unit concentration of polymer,  $\eta_{sp}/C$  is known as reduced viscosity and it depends upon the molecular weight of the polymer. Since,  $\eta_{sp}/C$  is dependent on concentration, the intrinsic viscosity,  $\eta_i$ , could be obtained by extrapolating the plot of  $\eta_{sp}/C$  to zero concentration,

$$\eta_i = \lim_{C \rightarrow 0} \eta_{sp}/C$$

Where 'C' is the concentration of the polymer in grams per 100 ml. Intrinsic viscosity values are expressed in dl/g.

The intrinsic viscosity of a polymer is related to its molecular weight by the following empirical relationship (Mark-Houwink equation):

$$\eta_{sp} = K M_v^a$$

where 'K' and 'a' are constants for a given type of polymer, solvent and at a given temperature and  $M_v$  represents the viscosity average molecular weight of the polymer.

The following Mark-Houwink equation was used to calculate the molecular weight of polymer.

For poly (methyl methacrylate) in benzene<sup>38</sup> at 30<sup>0</sup> C

$$\log \bar{P}_n = 1.32 \log [\eta_i] + 3.346$$

where  $\bar{P}_n$  is degree of polymerization.

#### 2.4 Synthesis of multi-site phase-transfer catalyst (MPTC) :

In a 250 mL three-necked round bottom flask, a measured quantity of one equivalent of pyrazine and four equivalent of hexadecyl bromide (1:4 molar ratios) was taken. To this mixture 40 mL of ethanol was added slowly and then the solution was stirred and refluxed under nitrogen atmosphere for 48 hours. After the reaction time, the excess solvent was removed by vacuum evaporator and thus formed disite PTC viz., 1,4-dihexadecylpyrazine-1,4-diium dibromide(MPTC). This in turn

was repeatedly washed with ether (4 x 25 mL) and dried and stored in a desiccator (Scheme 1). FT - IR (KBr,  $\text{cm}^{-1}$ ): 1178 ( $\text{C-N}^+$  stretching), 3106 (aromatic C-H stretching), 2932 (aliphatic C-H stretching), 1392 and 1473 (C-H bending);

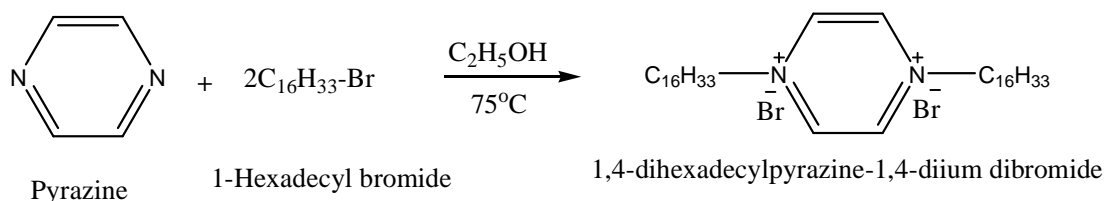
$^1\text{H}$  NMR (400  $\text{MHz}$ ,  $\text{CDCl}_3$ ):  $\delta$  7.33(2H),  $\delta$  5.51(2H),  $\delta$  4.18(2H),  $\delta$  3.59(2H),  $\delta$  3.28(2H),  $\delta$  1.80(2H),  $\delta$  1.73(2H),  $\delta$  1.19(2H),  $\delta$  1.11(16H),  $\delta$  0.75(3H);  $^{13}\text{C}$  NMR (100  $\text{MHz}$ ,  $\text{CDCl}_3$ ):  $\delta$  13.96, 18.26, 22.45, 22.50, 26.12, 28.05, 28.60, 28.80, 28.90, 30.10, 31.52, 31.62, 32.73, 34.03, 50.11, 53.05, 128.68; Elemental analysis Calc. C, 62.60 %; H, 10.21 %; N, 4.06 %. Found: C, 62.51 %; H, 10.11 %, N, 4.01 %.

*2.5 Polymerization procedure under sonocatalyzed condition :*

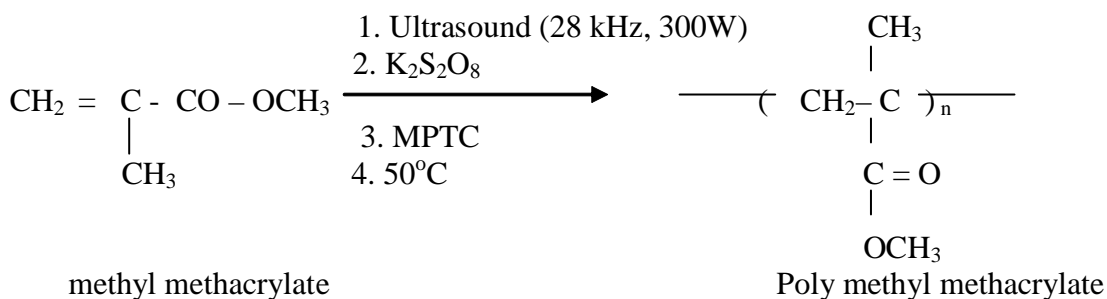
The polymerization reactions were carried out in an inert atmosphere at constant temperature of  $50^\circ\text{C}$  with ultrasonic energy (28 kHz, 300 W). The mixture consists of aqueous and organic phases. The monomer in ethyl acetate is the organic phase and the catalyst, potassium sulphate (for adjusting ionic strength) and sulphuric acid (for maintaining  $[\text{H}^+]$ ) were taken in aqueous phase. The reaction tube containing the reaction mixture was suspended at the center of the ultrasonic cleaning bath for 45 min to get the maximum ultrasound energy. When a calculated amount of initiator PDS was added to the reaction mixture, polymerization started and the polymer, poly MMA is precipitated continuously (scheme 2). The reaction was arrested by pouring the reaction mixture into ice-cold methanol containing traces of hydroquinone.

### Scheme 1

Synthesis of 1,4-dihexadecylpyrazine-1,4-dium dibromide (MPTC)



### Scheme 2



The polymer formed was filtered quantitatively through a sintered crucible (G-4), washed five times with distilled water and methanol, and dried at 50-60°C in a vacuum oven to constant weight. The rate of polymerization ( $R_p$ ) was calculated from the weight of the polymer obtained using the formula:

$$R_p = \frac{1000W}{V \times t \times M}$$

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

### 3. Results and Discussion

The polymerization of methyl methacrylate initiated by PDS–MPTC in ethyl acetate / water biphasic medium with ultrasonic energy (28 kHz, 300 W) was studied under different experimental conditions to evaluate the various parameters, which influence the polymerization reaction.

#### 3.1 Combined effect of ultrasound and steady state rate of polymerization :

The steady state rate of polymerization was ascertained by carrying out the polymerization of the monomer (methyl methacrylate) at different time intervals keeping the concentrations of monomer, initiator, MPTC, ionic strength and pH constant under ultrasound irradiation (28 kHz, 300W). The plot of  $R_p$  versus time shows a sharp increase to some extent, then slightly decreased and thereafter

remains constant. The time taken was found to be 50 minutes. When the same reaction was carried out in the absence of ultrasound, it was observed that the  $R_p$  was almost decreases 3 fold than with ultrasonic irradiation (Table 1, Fig. 1). It is due to the effect of ultrasound irradiation (28 kHz, 300 W) which can promote an intensive mixing of aqueous and organic phases, like homogenous solution.

#### 3.2 Ultrasonic Effect :

In the present work, we also investigate the effect of ultrasound on the polymerization of methyl methacrylate. Ultrasonic irradiation is defined as acoustic waves with frequencies in the 20 kHz-100 MHz range. Their energy creates cavities generating locally high temperature and pressure or strong electric fields. Ultrasound is known to accelerate diverse types of organic reactions of and it is established as an important technique in organic synthesis<sup>39,40</sup>. Heterogeneous reactions, which are otherwise slow due to poor mass transfer, are accelerated by sonification due to cavitation<sup>41</sup>. It was reported that a combination of PTC and ultrasound is often better than either of the two techniques alone<sup>40</sup>. In such cases the phase-transfer catalyst initiates the reaction by the transfer of species across the interface and ultrasound merely facilitates this transfer, possibly by increasing the interfacial area across which this transfer occurs.

All the experimental parameters were done at 28 kHz with output power of 300 W. The  $R_p$  also compared with 0 kHz and 40 kHz having same output power of 300W, using 1,4-dihexadecylpyrazine-1,4-diium dibromide (MPTC). The effect of the ultrasonic frequency

on the rate of polymerization ( $R_p$ ) was represented in Table 2. In our study at 50 min, in the presence of ultrasonic irradiation, the  $R_p$  of the reaction increased to almost three times and eight times faster for 28 kHz & 40 kHz than without ultrasonic irradiation *i.e.*, under silent condition. From these observations, it was inferred that the ultrasonic assisted multi-site phase-transfer catalyst significantly increased the rate of the polymerization. In addition, different ultrasonic frequencies induce various degrees of "cavity factor". A higher frequency induces a bigger size of cavity leading to a lower threshold to promote the reaction<sup>42-45</sup>. Hence, the  $R_p$  was increased by increasing the ultrasonic frequency in the order of 0 kHz > 28 kHz (300W) > 40 kHz (300W) for our system.

### 3.3 Effect of Temperature on $R_p$ :

The effect of variation of temperature in the range of 40-65°C on the polymerization was studied with ultrasonic effect (28 kHz, 300W) by keeping other variables constant. The  $R_p$  increases with the increase in temperature. It is obvious that the reactivity is increased with an increase in the temperature along with ultrasonic effect. The reason is that the number of reactant molecules which possess higher activation energy at higher temperature and thus the ultrasonic wave easily passes through the reactor. The collision of the reactants at higher temperature is also increased. Hence, the  $R_p$  is increased at higher temperature. Therefore as shown in Fig. 2, the  $R_p$  values are increased with an increase in temperature along with ultrasonic condition 28 kHz, 300W. From the slope of Arrhenius plot of  $5 + \log R_p$  vs  $1/T$  (Table 3, Fig. 2), the activation energy ( $E_a$ ) value for the polymerization reaction were

calculated. The other thermodynamic parameters (Table 4) such as entropy of activation ( $\Delta S^\ddagger$ ), enthalpy of activation ( $\Delta H^\ddagger$ ) and free energy of activation ( $\Delta G^\ddagger$ ) have been calculated using Eyring plot ( $\log R_p/T$  vs  $1/T$ ).

### 3.4 Effect of initiator concentration on $R_p$ :

The polymerization rate increased with increased concentration of  $K_2S_2O_8$  (PDS) in the range 0.01 – 0.08 mol.dm<sup>-3</sup> at a fixed concentration of MPTC, pH, monomer and ionic strength in combined with ultrasound wave (28 kHz and 300 W). A plot of  $5 + \log R_p$  vs  $1 + \log [PDS]$  was found to be linear with a slope of 0.48 (Fig. 3). The plot of  $R_p$  vs  $[PDS]$  is linear passing through the origin supporting the above deduction (Table 5, Fig. 4). A similar dependency of  $R_p$  order with respect to [initiator] has been reported by Balakrishnan et al in the presence of PTC-assisted free radical polymerization of methyl methacrylate<sup>46,47</sup>. The square-root dependency of  $R_p$  on  $[K_2S_2O_8]$  in the polymerization of EMA suggests that the induced decomposition of  $QS_2O_8$  is present and that the polymer radicals terminate by mutual bimolecular reaction. From the Table 2 and Fig. 2 and Fig. 3 shows that  $R_p$  value is almost 3 times higher in the presence of ultrasonic irradiation (28 kHz, 300 W) than without ultrasonication. It implies that the formation of  $QS_2O_8$  between PDS and MPTC may be enhanced in the presences of ultrasonic waves. The formed  $QS_2O_8$  is more lipophilic and hence it easily entered into the organic phase from aqueous phase where contain monomer. Thus the observed  $R_p$  value is more in the presence of ultrasonic waves. Therefore the monomer and

QS<sub>2</sub>O<sub>8</sub> are reacting rapidly and form more polymer. Further we also conducted the experiments with ultrasound (0 kHz), (28 kHz, 300W) and (40 kHz, 300W) in the absence of initiator. The results shows lower R<sub>p</sub> (almost 3 times) than with initiator by keeping other variables constant (Table 6).

### 3.5 Effect of [MPTC] on R<sub>p</sub> :

The dependence of R<sub>p</sub> on the concentration of MPTC was examined by varying MPTC in the range 0.01–0.08 mol.dm<sup>-3</sup> at fixed concentrations of monomer, PDS, pH and ionic strength and combined with ultrasound wave (28 kHz and 300W). A plot of (5+logR<sub>p</sub>) vs 1+log[MPTC], was found to be linear with a slope 0.49 (Fig. 5). The plot of R<sub>p</sub> vs [MPTC] passing through origin confirms the above observations (Table 7, Fig. 6). The increase in R<sub>p</sub> value is attributed to the change in the size, surface area and morphology of MPTC due to the positive effect of ultrasound might be enlarged. Further the collision between intermediates [QS<sub>2</sub>O<sub>8</sub>] is increased by increasing MPTC amount. Therefore the opportunity of forming a complex between them is largely increased. Hence, the R<sub>p</sub> increased with increase in the amount of MPTC. Choi *et al.*<sup>6</sup> reported that the polymerization rates leveled off at higher concentrations of crown ether in the bulk polymerization of methyl methacrylate (MMA) catalyzed by K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (PDS) as the water soluble initiator and 18-crown-6 (crown ether) as the phase-transfer catalyst.

### 3.6 Effect of monomer concentration on R<sub>p</sub>:

The effect of monomer concentration on R<sub>p</sub> was studied by varying the concentration

in the range 1.5 – 4.0 mol.dm<sup>-3</sup> at fixed concentrations of PDS, MPTC, pH and at constant ionic strength along with ultrasound wave energy (28 kHz and 300 W). From the plot of (5 + log R<sub>p</sub>) vs (1 + log [MMA]), the order of the reaction with respect to monomer concentration is found to be 0.99, almost unity (Fig. 7). The plot of R<sub>p</sub> against [MMA]<sup>1.0</sup> passing through the origin confirms the above observations (Table 8, Fig. 8). A similar order of unity has been observed by many other authors<sup>5,7,8</sup> in the phase-transfer catalyst assisted polymerization of vinylic monomers using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as the initiator. Balakrishnan et al observed second order dependence of R<sub>p</sub> on monomer concentration in the polymerization of MMA using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>- triethylbenzylammonium chloride (TEBA) system<sup>46</sup>.

### 3.7 Effect of acid [H<sup>+</sup>] and ionic strength (μ) on R<sub>p</sub> :

The effect of acid and ionic strength on the rate of polymerization was studied by varying H<sup>+</sup>, [H<sub>2</sub>SO<sub>4</sub>] and μ, [K<sub>2</sub>SO<sub>4</sub>] in the range of 0.001 - 0.002 mol.dm<sup>-3</sup> independently at definite concentrations of monomer, initiator and MPTC. Variation in either [H<sup>+</sup>] and μ of the medium have no discernible effect on R<sub>p</sub>.

### 3.8 Effect of volume fraction of aqueous on R<sub>p</sub> :

The effect of variation in the ratio of volume of aqueous phase (V<sub>w</sub>) to volume of organic phase (V<sub>o</sub>), V<sub>w</sub>/V<sub>o</sub>, on the R<sub>p</sub> was studied in the range of 0.61–1.00 under ultrasonic energy at 28 kHz, 300W at fixed concentrations of all other parameters. It was observed that

there is slight increase in the  $R_p$  with an increase in volume fraction of aqueous phase ratio (Vw). From the slope of linear plot of  $5 + \log R_p$  vs  $1 + \log (Vw/V_o)$  the reaction order with respect to (Vw/Vo) was found to be 0.19 (Table 9, Fig. 9). Balakrishnan *et al.*<sup>46</sup> observed the reaction exponents with respect to Vw/Vo in the polymerization of MMA in the range of 0.3-0.4 with  $K_2S_2O_8$  initiator with different phase transfer catalysts such as tetramethylammonium bromide (TMAB), tetraethylammonium bromide (TEAB) and triethylbenzylammonium chloride (TEBA). However, Simionescu and coworkers<sup>48</sup> reported an independent nature of  $R_p$  on Vw/Vo in the polymerization of MMA using  $K_2S_2O_8$  – Arquad phase-transfer catalyst system.

### 3.9 Effect of solvents on $R_p$ :

The effect of solvent on  $R_p$  was determined by carrying out the polymerization reaction of MMA in six different solvents such as cyclohexane, ethyl acetate, cyclohexanone, toluene, benzene and chlorobenzene under ultrasound irradiate condition. It was found that the  $R_p$  decreased in the following order: Cyclohexanone > chlorobenzene > ethyl acetate > toluene > benzene > cyclohexane

The decrease in the rate of polymerization may be due to the increase in the polarity of the medium, which facilitates greater transfer of  $QS_2O_8$  to the organic phase. The effect of the organic solvents on the  $R_p$  values with and without ultrasound conditions are shown in Table 10. Usually, the dielectric constants are used as the main index in choosing an appropriate organic solvent. The main reason is that the effect of the organic solvent involves

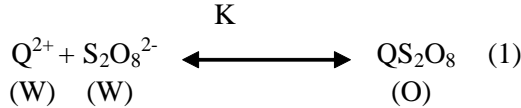
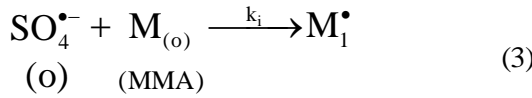
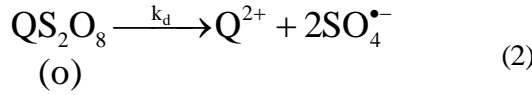
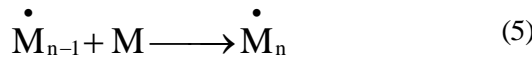
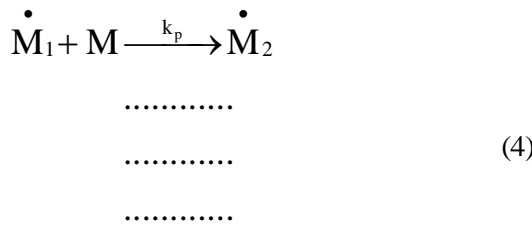
the solubility of the catalyst, transition state of the reaction, ion transfer, solvation and interfacial phenomena which are difficult to determine to a phase-transfer catalyst system. The ultrasonic irradiation can enhance the rate in the presence of more polar solvents due to passing higher ultrasonic waves to the reactor and makes fruitful collision between the reactants and hence we get higher  $R_p$  value for cyclohexanone solvent of this system<sup>49-52</sup>.

### 3.10 Molecular weight of Polymer :

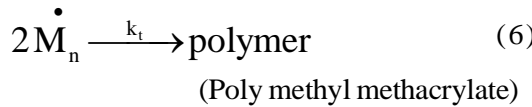
The molecular weight obtained by viscosity method of poly methyl methacrylate from different parameters such as variation of [MPTC], [PDS] and [MMA] was carried out at 35°C using ethyl acetate as solvent. The obtained polymer weight ( $2.9038 \times 10^5$ ) is almost same for the above said different experimental condition. The error range of viscosity measurement is found to be 0.2 %.

### 4. Mechanism and rate law :

In this investigation, potassium peroxydisulphate (PDS) which is a water soluble initiator is migrated from the aqueous phase to the monomer containing organic phase. This is facilitated by 1,4-dihexadecylpyrazine-1,4-diium dibromide which functions as a multi-site phase-transfer catalyst (MPTC). The quaternary ammonium salts transfer the  $S_2O_8^{2-}$  ion from aqueous phase to organic phase and enhances the rate of decomposition of  $S_2O_8^{2-}$  to sulphate ion radicals which initiates the polymerization. Based on the kinetic results the following mechanism has been proposed for the polymerization of methyl methacrylate (MMA).

**Phase Transfer****Initiation****Propagation**

(d) The termination occurs by the combination of two growing polymer chain radicals, it can be represented as



The subscripts (o) and (w) refer to organic phase and aqueous phase respectively. Applying the general aspects of free radical polymerization and stationary state hypothesis to the radical species, the rate law for this mechanism can be derived as follows:

The rate of initiation is given by

$$R_i = k_i [M][SO_4^{\bullet-}] \quad (7)$$

$$R_i = \frac{d[SO_4^{\bullet-}]}{dt} = 2k_d K [Q^{2+}]_w [S_2O_8^{2-}]_w \quad (8)$$

The rate of propagation is given by

$$R_p = k_p [\dot{M}] [M] \quad (9)$$

$$[\dot{M}] = \frac{R_p}{k_p [M]} \quad (10)$$

The rate of termination ( $R_t$ ) is given by

$$R_t = 2k_t [\dot{M}]^2 \quad (11)$$

At steady state, the rate of initiation equals to rate of termination *i.e.*,

$$R_i = R_t \quad (12)$$

$$2k_d K [Q^{2+}]_w [S_2O_8^{2-}]_w = 2k_t [M^{\bullet}]^2 \quad (13)$$

$$[\dot{M}]^2 = \frac{k_d K [Q^{2+}]_w [S_2O_8^{2-}]_w}{k_t} \quad (14)$$

$$[\dot{M}] = \left[ \frac{k_d K [Q^{2+}]_w [S_2O_8^{2-}]_w}{k_t} \right]^{\frac{1}{2}} \quad (15)$$

Using Eqs. 10 and 15, the rate of polymerization represented as follows.

$$R_p = k_p \left[ \frac{k_d K}{k_t} \right]^{\frac{1}{2}} [Q^{2+}]_w^{0.5} [S_2O_8^{2-}]_w^{0.5} [M]^{1.0} \quad (16)$$

The above equation satisfactorily explains all the experimental observations.

**Figure – 1.**  
**Steady State rate of polymerisation**

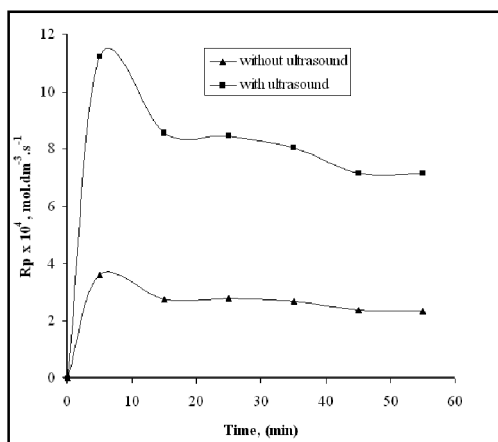


Fig 1. Reaction condition: [MMA], 2.5 mol.dm<sup>-3</sup>; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], 2.0 x 10<sup>-2</sup> mol.dm<sup>-3</sup>; [MPTC], 2.0 x 10<sup>-2</sup> mol.dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol.dm<sup>-3</sup>; [μ], 0.05 mol.dm<sup>-3</sup>; Temp. 50°C, ultrasound condition (28 kHz, 300 W).

**Figure 2. Effect of Temperature on Rp**

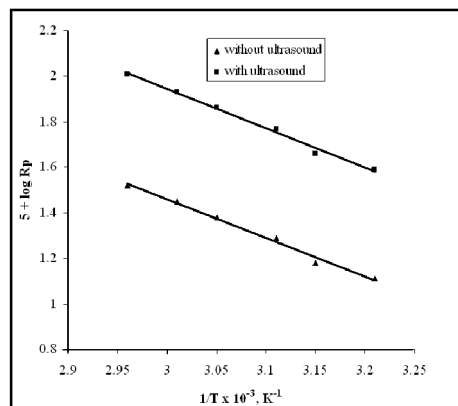


Fig 2. Reaction condition: [MMA], 2.5 mol.dm<sup>-3</sup>; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], 2.0 x 10<sup>-2</sup> mol.dm<sup>-3</sup>; [MPTC], 2.0 x 10<sup>-2</sup> mol.dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol.dm<sup>-3</sup>; [μ], 0.05 mol.dm<sup>-3</sup>; Time 50 min; ultrasound condition (28 kHz, 300 W).

**Figure 3. Effect of PDS concentration on Rp**

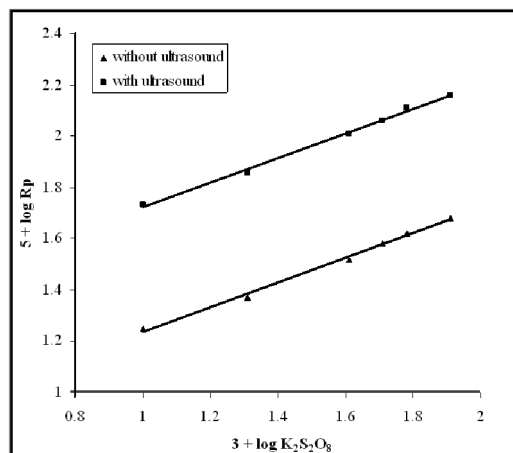


Fig 3. Reaction condition: [MMA], 2.5 mol.dm<sup>-3</sup>; [MPTC], 2.0 x 10<sup>-2</sup> mol.dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol.dm<sup>-3</sup>; [μ], 0.05 mol.dm<sup>-3</sup>; Temp. 50°C; Time, 50 min, ultrasound condition (28 kHz, 300 W).

**Figure 4. Effect of PDS concentration on Rp**

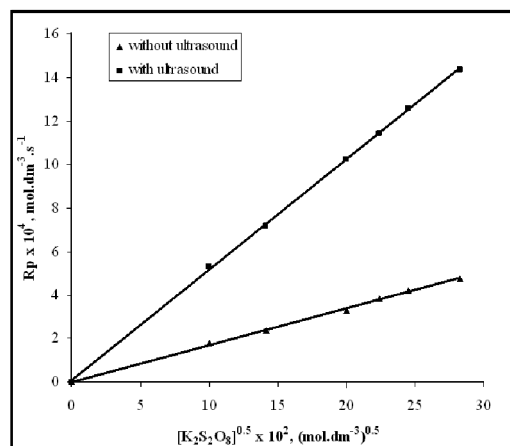


Fig 4. Reaction condition: [MMA], 2.5 mol.dm<sup>-3</sup>; [MPTC], 2.0 x 10<sup>-2</sup> mol.dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol.dm<sup>-3</sup>; [μ], 0.05 mol.dm<sup>-3</sup>; Temp. 50°C; Time, 50 min, ultrasound condition (28 kHz, 300 W).

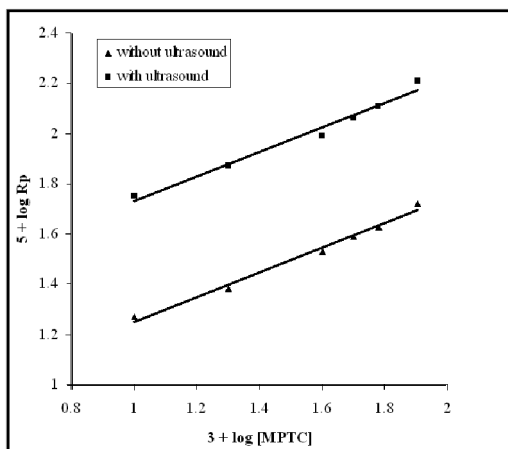
**Figure 5. Effect of MPTC concentration on Rp**

Fig 5. Reaction condition: [MMA],  $2.5 \text{ mol.dm}^{-3}$ ; [MPTC],  $2.0 \times 10^{-2} \text{ mol.dm}^{-3}$ ;  $[\text{H}^+]$ ,  $0.2 \text{ mol.dm}^{-3}$ ;  $[\mu]$ ,  $0.05 \text{ mol.dm}^{-3}$ ; Temp.  $50^\circ\text{C}$ ; Time, 50 min, ultrasound condition (28 kHz, 300 W).

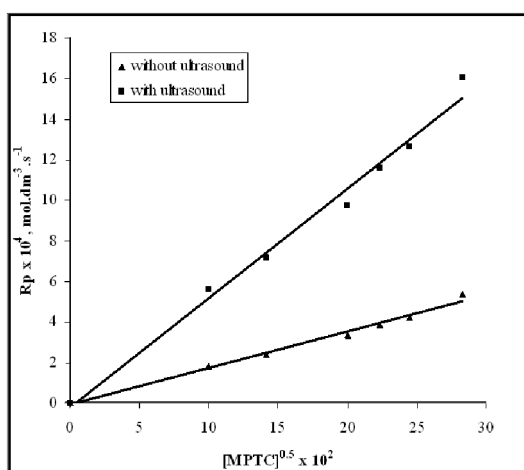
**Figure 6. Effect of MPTC concentration on Rp**

Fig 6. Reaction condition: [MMA],  $2.5 \text{ mol.dm}^{-3}$ ; [MPTC],  $2.0 \times 10^{-2} \text{ mol.dm}^{-3}$ ;  $[\text{H}^+]$ ,  $0.2 \text{ mol.dm}^{-3}$ ;  $[\mu]$ ,  $0.05 \text{ mol.dm}^{-3}$ ; Temp.  $50^\circ\text{C}$ ; Time, 50 min, ultrasound condition (28 kHz, 300 W).

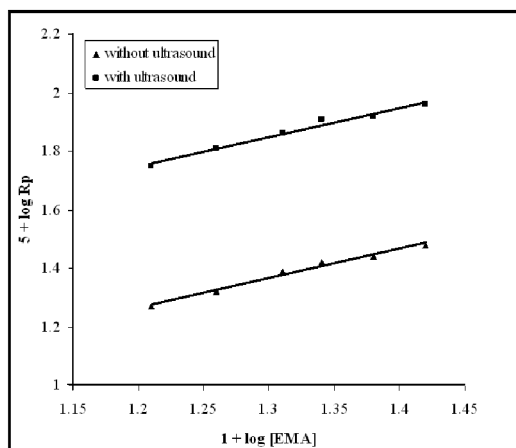
**Figure 7. Effect of monomer concentration on Rp**

Fig 7. Reaction condition:  $[\text{K}_2\text{S}_2\text{O}_8]$ ,  $2.5 \times 10^{-2} \text{ mol.dm}^{-3}$ ; [MPTC],  $2.0 \times 10^{-2} \text{ mol.dm}^{-3}$ ;  $[\text{H}^+]$ ,  $0.2 \text{ mol.dm}^{-3}$ ;  $[\mu]$ ,  $0.05 \text{ mol.dm}^{-3}$ ; Temp.  $50^\circ\text{C}$ ; Time, 50 min, ultrasound condition (28 kHz, 300 W).

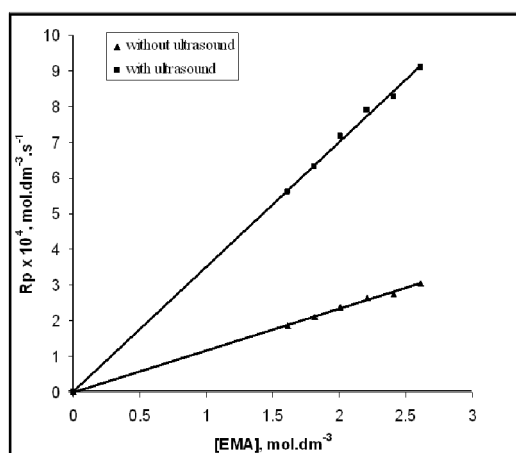
**Figure 8. Effect of monomer concentration on Rp**

Fig 8. Reaction condition:  $[\text{K}_2\text{S}_2\text{O}_8]$ ,  $2.5 \times 10^{-2} \text{ mol.dm}^{-3}$ ; [MPTC],  $2.0 \times 10^{-2} \text{ mol.dm}^{-3}$ ;  $[\text{H}^+]$ ,  $0.2 \text{ mol.dm}^{-3}$ ;  $[\mu]$ ,  $0.05 \text{ mol.dm}^{-3}$ ; Temp.  $50^\circ\text{C}$ ; Time, 50 min, ultrasound condition (28 kHz, 300 W).

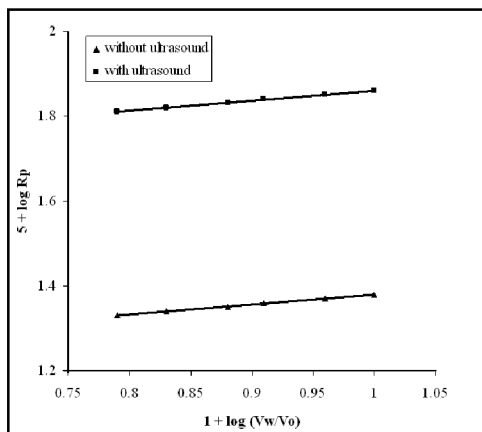
**Figure 9. Effect of aqueous phase volume on Rp**

Fig 9. Reaction condition : [MMA], 2.5 mol.dm<sup>-3</sup>; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], 2.0 x 10<sup>-2</sup> mol.dm<sup>-3</sup>; [MPTC], 2.0 x 10<sup>-2</sup> mol.dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol. dm<sup>-3</sup>; [μ], 0.05 mol.dm<sup>-3</sup>; Temp, 50°C; Time 45 min, ultrasound condition (28 kHz, 300 W).

**Table 1. Steady State rate of polymerisation**

Time (min)	Rp x 10 <sup>4</sup> , mol. dm <sup>-3</sup> .s <sup>-1</sup> (without ultrasound)	Rp x 10 <sup>4</sup> , mol.dm <sup>-3</sup> .s <sup>-1</sup> (with ultrasound)
5	3.9953	11.8924
15	3.6124	10.9826
25	2.8646	9.6524
35	2.8328	9.2529
45	2.6326	8.6832
50	2.5952	8.1038
55	2.5869	8.1024

Reaction condition: [MMA], 2.5 mol dm<sup>-3</sup>; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], 2.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>; [MPTC], 2.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol dm<sup>-3</sup>; [μ], 0.05 mol dm<sup>-3</sup>; Temp, 50°C; ultrasound condition (28 kHz, 300 W).

**Table 2. Ultrasonic Effect**

0 kHz Rp x 10 <sup>4</sup> , mol. dm <sup>-3</sup> .s <sup>-1</sup>	28 kHz Rp x 10 <sup>4</sup> , mol. dm <sup>-3</sup> .s <sup>-1</sup>	40 kHz Rp x 10 <sup>4</sup> , mol. dm <sup>-3</sup> .s <sup>-1</sup>
2.59	8.10	17.25

Reaction condition: [MMA], 2.5 mol dm<sup>-3</sup>; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], 2.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>; [MPTC], 2.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol dm<sup>-3</sup>; [μ], 0.05 mol dm<sup>-3</sup>; Temp, 50°C, Time, 50 min

**Table 3. Effect of Temperature on Rp**

Temperature, K	Rp x 10 <sup>4</sup> , mol dm <sup>-3</sup> s <sup>-1</sup> (without ultrasound)	Rp x 10 <sup>4</sup> , mol dm <sup>-3</sup> s <sup>-1</sup> (with ultrasound)	1/T x 10 <sup>3</sup> , K <sup>-1</sup>	5 + log Rp (without ultrasound)	5 + log Rp (with ultrasound)
313	1.8081	5.9592	3.1949	1.2572	1.7751
318	2.1763	6.8075	3.1447	1.3377	1.8330
323	2.5901	8.1056	3.0960	1.4133	1.9088
328	2.8438	8.8971	3.0488	1.4539	1.9492
333	3.2991	9.5241	3.0030	1.5184	1.9788
338	3.9762	10.0268	2.9586	1.5995	2.0012

Reaction condition : [MMA], 2.5 mol dm<sup>-3</sup>; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], 2.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>; [MPTC], 2.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol dm<sup>-3</sup>; [μ], 0.05 mol dm<sup>-3</sup>; Time 50 min; ultrasound condition (28 kHz, 300 W).

Table 4. Thermodynamic Parameters

Ea, kJ / mol	$\Delta G^\ddagger$ , kJ/mol	$\Delta H^\ddagger$ , kJ /mol	$\Delta S^\ddagger$ , eu
27.26	76.01	25.37	-156.78

Reaction condition : [MMA], 2.5 mol dm<sup>-3</sup>; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], 2.0 x10<sup>-2</sup> mol dm<sup>-3</sup>; [MPTC], 2.0 x10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol dm<sup>-3</sup>; [μ], 0.05 mol dm<sup>-3</sup>; Time 50 min; ultrasound condition (28 kHz, 300 W).

Table 5. Effect of PDS concentration on Rp

[K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] x 10 <sup>2</sup> , mol.dm <sup>-3</sup>	[K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] <sup>0.5</sup> x10 <sup>2</sup> (mol.dm <sup>-3</sup> ) <sup>0.5</sup>	Rp x 10 <sup>4</sup> , mol.dm <sup>-3</sup> .s <sup>-1</sup> (without ultrasound)	Rp x 10 <sup>4</sup> , mol.dm <sup>-3</sup> .s <sup>-1</sup> (with ultrasound)	3+ log [K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ]	5 + log Rp (without ultrasound)	5 + log Rp (with ultrasound)
1	10.01	1.8636	5.2578	1.0000	1.2704	1.7208
2	14.14	2.5921	8.0835	1.3010	1.4137	1.9076
4	20.01	3.5208	10.2023	1.6021	1.5466	2.0087
5	22.36	3.8702	11.2694	1.6990	1.5877	2.0519
6	24.49	4.4486	12.9658	1.7782	1.6482	2.1128
8	28.28	5.1586	14.9589	1.9031	1.7125	2.1749

Reaction condition : [MMA] , 2.5 mol dm<sup>-3</sup>; [MPTC], 2.0 x10<sup>-2</sup> mol dm<sup>-3</sup> [H<sup>+</sup>], 0.2 mol dm<sup>-3</sup>; [μ], 0.05 mol dm<sup>-3</sup>; Temp, 50° C; Time, 50 min; ultrasound condition (28 kHz, 300 W).

Table 6. Ultrasonic Effect without initiator

0 kHz Rp x 10 <sup>4</sup> , mol. dm <sup>-3</sup> .s <sup>-1</sup>	28 kHz Rp x 10 <sup>4</sup> , mol. dm <sup>-3</sup> .s <sup>-1</sup>	40 kHz Rp x 10 <sup>4</sup> , mol. dm <sup>-3</sup> .s <sup>-1</sup>
0.925	2.89	6.16

Reaction condition: [MMA], 2.5 mol.dm<sup>-3</sup>; [MPTC], 2.0 x10<sup>-2</sup> mol.dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol.dm<sup>-3</sup>; [μ], 0.05 mol.dm<sup>-3</sup>; Temp. 50°C, Time 50 min.

Table 7. Effect of MPTC concentration on Rp

[MPTC] x10 <sup>2</sup> , mol.dm <sup>-3</sup>	[MPTC] <sup>0.5</sup> x10 <sup>2</sup> (mol.dm <sup>-3</sup> ) <sup>0.5</sup>	Rp X 10 <sup>4</sup> , mol.dm <sup>-3</sup> .s <sup>-1</sup> (without ultrasound)	Rp X 10 <sup>4</sup> , mol.dm <sup>-3</sup> .s <sup>-1</sup> (with ultrasound)	3+ log [MPTC]	5+ log Rp (without ultrasound)	5+ log Rp (with ultrasound)
1	10.01	2.0133	5.8386	1.0000	1.3039	1.7663
2	14.14	2.5906	7.5127	1.3010	1.4134	1.8758
4	20.01	3.7282	10.8118	1.6021	1.5715	2.0339
5	22.36	4.1629	12.0724	1.6990	1.6194	2.0818
6	24.49	4.6827	13.5798	1.7782	1.6705	2.1329
8	28.28	5.6273	16.3192	1.9031	1.7503	2.2127

Reaction condition : [MMA], 2.5 mol dm<sup>-3</sup>; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], 2.0 x10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol dm<sup>-3</sup>; [μ], 0.05 mol dm<sup>-3</sup>; Temp, 50° C; Time, 50 min; ultrasound condition (28 kHz, 300 W).

Table 8. Effect of monomer concentration on Rp

[MMA], mol.dm <sup>-3</sup>	Rp x 10 <sup>4</sup> , mol.dm <sup>-3</sup> .s <sup>-1</sup> (without ultrasound)	Rp x 10 <sup>4</sup> , mol.dm <sup>-3</sup> .s <sup>-1</sup> (with ultrasound)	1+ log [MMA]	5 + log Rp (without ultrasound)	5 + log Rp (with ultrasound)
1.5	1.5424	4.7814	1.1761	1.1882	1.6796
2	2.0342	6.3060	1.3010	1.3084	1.7998
2.5	2.5936	8.1042	1.3979	1.4139	1.9087
3	2.8255	8.7591	1.4771	1.4511	1.9425
3.5	3.3692	10.4445	1.5441	1.5275	2.0189
4	4.3232	13.4032	1.6021	1.6358	2.1272

Reaction condition : [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], 2.0 x10<sup>-2</sup> mol dm<sup>-3</sup>; [MPTC], 2.0 x10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol dm<sup>-3</sup>; [μ], 0.05 mol dm<sup>-3</sup>; Temp, 50° C; Time, 50 min; ultrasound condition (28 kHz, 300 W).

Table 9. Effect of aqueous phase volume on Rp

Vw/ Vo	1+ log (Vw/Vo)	Rp x 10 <sup>4</sup> mol dm <sup>-3</sup> .s <sup>-1</sup> (without ultrasound)	Rp x 10 <sup>4</sup> mol dm <sup>-3</sup> .s <sup>-1</sup> (with ultrasound)	5 + log Rp (without ultrasound)	5 + log Rp (with ultrasound)
0.61	0.7853	2.1837	6.5993	1.3392	1.8195
0.67	0.8261	2.2940	7.1647	1.3606	1.8552
0.75	0.8751	2.3747	7.2711	1.3756	1.8616
0.82	0.9138	2.4638	7.4611	1.3916	1.8728
0.92	0.9638	2.5657	7.6296	1.4092	1.8825
1	1.0000	2.5906	8.1077	1.4134	1.9089

Reaction condition : [MMA], 2.5 mol dm<sup>-3</sup>; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], 2.0 x10<sup>-2</sup> mol dm<sup>-3</sup>; [MPTC], 2.0 x10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol dm<sup>-3</sup>; [μ], 0.05 mol dm<sup>-3</sup>; Temp, 50° C; Time 50 min; ultrasound condition (28 kHz, 300 W).

Table 10. Effect of solvent polarity on Rp

Rp x 10 <sup>4</sup> , mol.dm <sup>-3</sup> .s <sup>-1</sup>	Solvents					
	Cyclohexanone (18.3)*	Chlorobenzene (5.7)*	Ethyl Acetate (3.91)*	Toluene (2.5)*	Benzene (2.4)*	Cyclohexane (1.13)*
With ultrasound	14.17	11.14	8.12	5.84	5.19	3.07
Without ultrasound	5.06	3.98	2.59	2.06	1.89	1.11

Reaction condition: [MMA], 2.5 mol dm<sup>-3</sup>; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], 2.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>; [MPTC], 2.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>], 0.2 mol dm<sup>-3</sup>; [μ], 0.05 mol dm<sup>-3</sup>; Time, 50 min, Temp, 50°C; ultrasound condition (28 kHz, 300 W).

\* Dielectric constant

## Conclusion

In this study, a novel dual-site phase-transfer catalyst, viz., 1,4-dihexadecylpyrazine-1,4-diium dibromide was prepared and it was used to conduct the free radical polymerization of methyl methacrylate by ultrasound assisted phase-transfer catalysis in ethyl acetate/water biphasic system at 50 ± 1°C under inert atmosphere. The parameters influencing the rate of polymerization were performed with and without ultrasound irradiation. It shows that the Rp enhanced almost 3 fold and 8 fold with 28 kHz (300W) and 40 kHz (300W) under ultrasound irradiation condition compared with without ultrasound condition. The Rp value increases with increasing the [monomer], [initiator], [MPTC] and temperature. From the Arrhenius plot the energy of activation Ea, and other thermodynamic parameters such as entropy of activation (ΔS<sup>#</sup>), enthalpy of activation (ΔH<sup>#</sup>) and free energy of activation (ΔG<sup>#</sup>) have been calculated. Based on the kinetic results, a suitable mechanism has been proposed.

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