Radical polymerization of benzyl methacrylate under unstirred ultrasonic irradiation with a new multi-site phase-transfer catalyst - A kinetic study

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Abstract

The kinetics of phase-transfer catalyzed radical polymerization of benzyl methacrylate (BMA) using potassium proxydisulphate (PDS) as water soluble initiator and 1,4-dihexadecylbenzopyrazine-1,4-diium bromide as multi site phase-transfer catalyst(MPTC) has been investigated in ethyl acetate / water two phase system assisted by ultrasound irradiation at constant temperature $70 \pm 1°C$ under nitrogen atmosphere. The rate of polymerization increases with an increase in concentrations of BMA, PTC and PDS. The order with respect to [BMA], [MPTC], and [PDS] were found to be 1.019, 1.098 and 0.502 respectively. Based on the observed results a suitable mechanism has been proposed to account for the experimental observations followed by a discussion on its significance.

Keywords: Benzyl methacrylate, Benzopyrazine, hexadecyl bromide, multi-site phase- transfer catalyst.

Highlights

1. Preparation of a new multi-site phase-transfer catalyst (MPTC).
2. MPTC was used for the polymerization of Benzyl methacrylate.
3. Combined effect of ultrasound with various kinetic parameters were studied

4. The effect of different ultrasound frequency was compared for the rate of polymerization of the reaction.

5. The rate of polymerization enhanced almost 3 fold and 8 fold with frequency range of 28 kHz, 40 kHz with the same output power of 300W.

1. Introduction

The reaction between insoluble and mutually immiscible reactants can be effectively carried out by employing Phase-Transfer Catalytic technique under mild conditions to get high conversion and product selectivity. PTC plays a key role in carrying out reaction between immiscible lipophilic and hydrophilic reactants. This technique is employed in the manufacturing processes of a host of specialty chemicals including monomers for polymer synthesis[1-5]. It is reported that polymerization of water insoluble monomers in the presence of water soluble initiator can be carried out with PTC. In the presence of a PTC the monomer in the organic phase reacts with the initiator in the aqueous phase[6-14]. The reaction is achieved by means of PTC which complexes and stabilizes the water soluble initiator into the organic phase. However because of the difficulty faced in their recovery and reuse, it has received poor attention from researchers. In fact several researchers have devoted their attention for the development of new soluble and insoluble MPTC since they are found to enhance the reaction especially in bi-phasic systems. Various MPTCs have been synthesized and reported for a large number of organic and polymerization reactions.

In recent years organic reactions are carried out assisted by ultrasonic irradiation due to its various advantages. The technique of use of ultrasonic irradiation is convenient, economical and also eco-friendly. Although sonication techniques have been initially applied to homogeneous reactions in a variety of solvents, this approach had now evolved into a useful technique in heterogeneous reactions also[15-25].

A survey of the literature reveals that no systematic investigation of the kinetics and mechanism of polymerization for aromatic vinylic monomers with $K_2S_2O_8$ aided by ultrasonic irradiation have been carried out. Hence in order to study the effect of ultrasonic irradiated polymerization of BMA in the presence of the newly synthesized MPTC, this work has been carried out.

2. Experimental

Benzopyrazine (Aldrich – USA), BMA (Aldrich – USA) was washed with 2% NaOH solution to remove inhibitor (HCl) and again washed with double distilled water to remove the basic impurities. The samples of potassium perdisulphate (Nice Chemicals – India) and hexadecyl bromide (SRL) were obtained from a leading delar and other chemicals were used as received. Polymerization studies were carried out in long Pyrex tubes (4 cm X 20 cm) of about 100 ml capacity with a B-24 quick fit socket fitted with a B-24 cone with a provision for inlet and outlet terminals in order to isolate the reactive mixture from atmospheric oxygen. All other experiments were conducted in a thermostat bath of 25 liter capacity. The

temperature of the bath was controlled by a hot wire vacuum switch relay to an accuracy of $\pm$ 0.1°C. Water in the bath was heated electrically and stirred well by mechanical stirrer for maintaining constant temperature through out the bath. Experiments were carried out in the temperature range 55 - 80°C. Nitrogen gas used for deaeration was freed from trace of oxygen and other impurities by passing through four vertical glass tubes containing separately (i) Fieser's solution (ii) lead acetate solution (iii) Potassium hydroxide solution and (iv) Distilled water. The FT-IR spectra were recorded on a Bruker-Tensor27 FT-IR spectrophotometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 500 MHZ and 125 MHZ spectrometer. Elemental analysis was performed on a Perkin-Elmer 240B elemental analyzer.

### 2.1 Ultrasonic process equipment :

Ultrasonic energy is transmitted to the reaction vessel through the liquid medium, usually water in the tank. For safety purpose, the sonochemical reactor consisted of two layers of stainless steel sheet. The sonochemical reactor configuration used in the present work is basically an ultrasonic bath with 5 litre capacity. The reactor has an operating frequency of 28 kHz and 40 kHz both with an output of 300 W. The 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 provides the facility for continuous operation of the process. 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 conditions. From the top of the sonicator, if the water level is lower than the outlet *i.e.*, 3 cm below the applied frequency is automatically cut off. So the water fill is important. The reactor is made of Pyrex glass polymer tube fitted with an inlet and outlet for nitrogen. An inert atmosphere is maintained inside the reaction tubes by closing the inlet and outlet with rubber gaskets. This reaction vessel is 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 Polymerization procedure under sonocatalyzed condition :

The reaction tubes for the polymerization are long Pyrex glass tubes with inlet and outlet for nitrogen gas. The polymerization reactions are carried out in an inert atmosphere at constant temperature of 70°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 phase-transfer catalyst, potassium perdisulphate, potassiumsulphate (for adjusting ionic strength) and sulphuric acid (for maintaining [H$^+$]) were taken in aqueous phase. The reaction tube containing the reaction mixture is suspended at the center of the ultrasonic cleaning bath for 50 min to get the maximum ultrasound energy. The reaction is arrested by pouring the reaction mixture into ice-cold methanol containing traces of hydroquinone.

The polymer formed was filtered quantitatively through a sintered crucible (G-4)

Scheme-1

Benzyl methacrylate   Polybenzyl methacrylate

Scheme-2

benzo pyrazine   1-Hexadecayl   1,4-dihexadecyl benzopyrazine-1,4-
                    bromide   diium dibromide (MPTC)
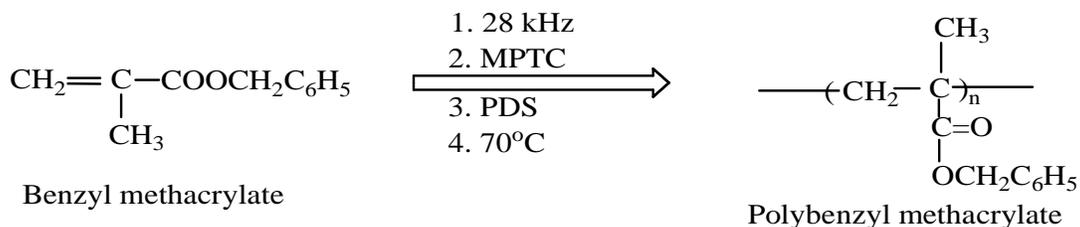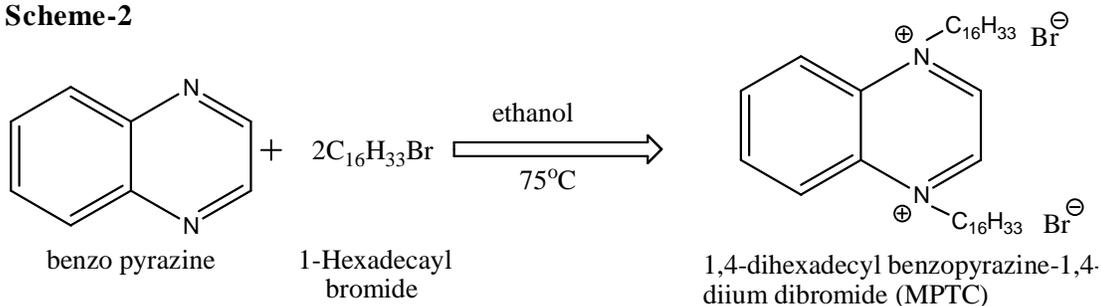
washed several times with distilled water and methanol, and dried at 60-70°C in a vacuum oven to constant weight (scheme-1). The rate of polymerization (Rp) was determined gravimetrically. The Rp was calculated from the weight of the polymer obtained using the formula:

$$R_p = \frac{1000\,W}{v\,t\,m}$$

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
       (benzyl methacrylate)

2.3 Synthesis of multi-site phase transfer catalyst :

    Measured quantity of one equivalent Benzopyrazine dissolved in 20 ml of C_2H_5OH is taken in 250 ml two neck R_B flask. Two equivalent hexadecyl bromide is then introduced in the flask. The mixture is heated slowly for several hours. After removal of all C_2H_5OH, crystals of 1,4-dihexadecylbenzopyrazine-1,4-diium bromide(MPTC) (scheme-2) is obtained. When washed with ether white crystals of MPTC is obtained.

The experimental analysis data are quite satisfactory.

^{1}H NMR (500 MHz, D_2O); δ 8.84 (2H), δ 7.33 (4H), δ 5.52 (2H), δ 4.16 (2H), δ 3.58 (2H), δ 3.28 (2H), δ 1.82 (2H), δ 1.73 (2H), δ 1.19 (2H), δ 1.11 (16H), δ 0.75 (3H).

^{13}C NMR (125 MHz, D$_2$O); δ 13.94, 18.26, 22.42, 22.51, 26.14, 28.04, 28.62, 28.84, 28.91, 30.11, 31.52, 31.59, 32.74, 34.03, 50.12, 53.05, 118.72, 127.41, 128.54, 145.61. FT-IR (KBr, cm^{-1}); 1182 (C-N$^+$ stretching), 2932 (aliphatic C-H stretching).

3. Results and Discussion

The polymerization of benzylmethacrylate initiated by PDS–MPTC in ethyl acetate /water biphase medium with ultrasonic energy (28 kHz, 300W) 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 :

Polymerisation reactions were carried out at different time duration with fixed concentrations of BMA,MPTC, K$_2$S$_2$O$_8$, H$^+$, K$_2$SO$_4$ and ionic strength to determine the steady state of polymerisation. Experimental data show that the rate of polymerisation increases initially with time, reaches the maximum and then decreases sharply to finally attain a constant value (Table 1). A plot is drawn between Rp and Time to determine the steady state rate of polymerization. It has been found from the plot [Fig. 1] that the steady state rate Polymerisation is attained at about 50 min. So polymerisation was carried out 50 min duration to study the effect of other parameters.

3.2 Ultrasonic Energy :

In the present work, we investigate the effect of ultrasound on the polymerization of benzyl methacrylate. Ultrasound 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. Heterogeneous reactions, which are otherwise slow due to poor mass transfer, are accelerated by signification due to cavitations. It was reported that a combination of PTC and ultrasound is often better than either of the two techniques alone. 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 reaction rate also compared with 0 kHz and 40 kHz having same output power of 300W, using 1,4-dihexadecylbenzopyrazine-1,4-diium bromide (MPTC) as a phase-transfer catalyst. The effect of the ultrasonic frequency on the rate of polymerization (Rp) was represented in Table 2. In our study at 50 min, in the presence of ultrasonic irradiation, the Rp 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 phase-transfer catalyst significantly increased the rate of the polymerization. A higher frequency induces a bigger size of cavity leading to a lower threshold to promote the reaction. Hence, the Rp was increased by increasing the ultrasonic frequency in the order of 40 kHz (300W) > 28 kHz (300W) > 0 kHz for our system.

3.3 The effect of [BMA] on Rp :

The effect of [BMA] on Rp was studied by conducting polymerisation with different concentrations of BMA while keeping fixed the concentrations of other components (Table 3). It has been found that the Rp increased with increase in [BMA]. The plot of log [BMA] against log Rp was a straight with a slope of 1.019 [Fig. 2]. The reaction order of 1.019 with respect to [BMA] is further confirmed from the straight line passing through the origin plotted between [BMA] vs Rp. [Fig. 3]. Vajiravel *et al.*, reported a first order dependence of Rp on concentration of glycidyl methacrylate in the presence of $K_2S_2O_8$ as a initiator[26].

3.4 Effect of [MPTC] on Rp :

It has been found that increasing the concentration of MPTC increases the value of Rp in the employed concentration range from 0.02 to 0.12 mol.dm^{-3} [Table 4]. From the plot 2+log[MPTC] vs 6+log Rp. The slope was found to be 1.0. [Fig. 4]. A straight line passing through the origin in the plot of Rp vs [MPTC] confirms the observed order of 1.0 [Fig. 5]. Gupta and Mandal[27,28] also reported a first order dependence of Rp on concentration of tetrabutylammonium bromide (PTC) for the polymerization of methylmethacrylate in the presence of $K_2S_2O_8$ in ethyl acetate/water media. The number of carbon atom in MPTC increases the libophilic nature which accelerate Rp.

3.5 Effect of [PDS] on Rp :

The effect on Rp of varying the concentration of $K_2S_2O_8$ was observed by varying concentration in the range of 0.02 to 0.12 mol.dm^{-3} at a fixed concentration of BMA,MPTC,H$^+$ and ionic strength [Table 5]. It is found that Rp increase with increase in the concentration of PDS. A plot of logRp vs log $[K_2S_2O_8]$ is linear with a slope of 0.5, indicating the half order dependence of Rp on $K_2S_2O_8$ [Fig. 6]. This is supported by a straight line passing through origin in the plot of Rp vs $[K_2S_2O_8]$ [Fig. 7].

3.6 Effect of various catalysts on Rp :

Quaternary ammonium salts are generally used as phase-transfer catalysts to promote reaction rate. In addition to ultrasound irradiation condition along with 1,4-dihexadecyl-1,4- diium dibromide (MPTC) four other single site quaternary ammonium salts, such as terahexylammonium chloride (THAC), tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB), and tetrabutylammonium iodide (TBAI), were investigated to test their reactivities. The experimental results are listed in (Table 6). The reactivity of the PTC depends on its degree of hydration and on the structure of its counter cation (Q^+). A comparison among MPTC, THAC, TBAC, TBAB, and TBAI reveals that the more lipophilic of the quaternary ammonium cation, the greater the effectiveness in transferring sulphate radical anion ($SO_4^{.-}$) into the organic media. In other words, the catalytic activities are mainly due to the solubility's of their ion-pair *i.e.*, $Q^+SO_4^{.-}$. In the organic phase which turn can be attributed to the nature and bulkiness of Q^+ and the medium. The reactivity of TBAC, TBAB, and TBAI are not affected significantly by the sulphate anion radical, with the symmetric tetrabutylammonium cation (Q^+). 1,4-dihexa-

decylbenzopyrazine-1,4-diium bromide (MPTC) is more reactive than the other quaternary salts even though it have symmetric cation nature, due to its lipophilic nature may be higher. The activity of the lipophilic cation Q^+ is determined mainly by two factors, its extractability which is depends on organophilicity of the catalyst and the anion radical pairs $(Q^+SO_4^{\cdot-})$ between the organic phase and aqueous phase. Based on the above arguments the order of the reactivities of these quaternary ammonium salts are in order MPTC> THAC > TBAC > TBAB > TBAI.

3.7 Effect of solvent on Rp :

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

cyclohexanone > chlorobenzene > ethyl acetate > dibutyl ether > toluene > cyclohexane.

The decrease in the rate of polymerization may be due to the decrease in the polarity of the medium. The effect of the organic solvents on the Rp values with and without ultrasound conditions are shown in Table 7. 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 Rp value for cyclohexanone solvent of this system.

Table 1. Steady state rate on Rp

Time (min)	$Rp \times 10^5$, mol.dm^{-3}.s^{-1} (Without ultrasound)	$Rp \times 10^5$, mol.dm^{-3}.s^{-1} (With ultrasound)
10	1.3214	4.2760
20	1.1216	3.6876
30	0.9878	3.3042
40	0.9654	3.1260
50	0.9378	2.9072
60	0.9352	2.8692
70	0.9310	2.7868

Reaction condition: [BMA], 0.9378 mol.dm^{-3}; [PDS],2.0×10^{-2} mol.dm^{-3}; [MPTC], 2.0×10^{-2} mol.dm^{-3}; [H$^+$], 0.2 mol.dm^{-3}; [μ], 0.05 mol.dm^{-3}; Temp. 70°C, ultrasound condition (28 kHz, 300 W).

Table 2. Ultrasonic Effect

0 kHz $Rp \times 10^5$, mol.dm^{-3}.s^{-1}	28 kHz $Rp \times 10^5$, mol.dm^{-3}.s^{-1}	40 kHz $Rp \times 10^5$, mol.dm^{-3}.s^{-1}
0.9378	2.9072	7.2464

Reaction condition: [BMA], 0.9378 mol.dm^{-3}; [PDS], 2.0×10^{-2} mol.dm^{-3}; [MPTC], 2.0×10^{-2} mol.dm^{-3}; [H$^+$], 0.2 mol.dm^{-3}; [μ], 0.05 mol.dm^{-3}; Temp. 70°C, Time, 50 min.

Table 3. Effect of [BMA] on Rp

[BMA] mol,dm^{-3}	Rp x10^5 mol.dm^{-3}.s^{-1} (without ultrasound)	Rp x10^5 mol.dm^{-3}.s^{-1} (with ultrasound)	2 + log [BMA]	6 + log Rp (without ultrasound)	6 + log Rp (with ultrasound)
0.2951	0.9378	2.9072	1.4699	1.9721	2.4634
0.5902	1.9012	5.9317	1.7710	2.2790	2.7732
0.8853	2.8453	8.7920	1.9471	2.4541	2.9440
1.1804	3.8881	12.0920	2.0720	2.5897	3.0825
1.4755	4.7469	14.6216	2.1689	2.6764	3.1650
1.7706	5.8847	18.3602	2.2481	2.7694	3.2638

Reaction condition: [PDS], 2.0×10^{-2} mol.dm^{-3}; [MPTC], 2.0×10^{-2} mol.dm^{-3}; [H$^+$], 0.2 mol.dm^{-3}; [μ], 0.05 mol.dm^{-3}; Temp. 70°C, Time, 50 min; ultrasound condition (28 kHz, 300 W).

Table 4. Effect of [MPTC] on Rp

[MPTC]x10^2 mol,dm^{-3}	Rp x10^5 mol.dm^{-3}.s^{-1} (without ultrasound)	Rp x10^5 mol.dm^{-3}.s^{-1} (with ultrasound)	2 + log [MPTC]	6 + log Rp (without ultrasound)	6 + log Rp (with ultrasound)
2	0.9378	2.9072	1.3010	1.9721	2.4620
4	2.1381	6.6085	1.6010	2.1646	2.8201
6	3.7429	11.6407	1.7781	2.2033	3.0660
8	4.7120	14.5553	1.9030	2.2553	3.1630
10	5.4088	16.7672	2.0000	2.3553	3.2244
12	6.7936	21.0601	2.0792	2.3713	3.3234

Reaction condition: [BMA], 0.2951 mol.dm^{-3}; [PDS], 2.0×10^{-2} mol.dm^{-3};
[H$^+$], 0.2 mol.dm^{-3}; [μ], 0.05 mol.dm^{-3}; Temp. 70°C, Time, 50 min; ultrasound condition (28 kHz, 300 W).

Table 5. Effect of [PDS] on Rp

[PDS] x10^2 mol,dm^{-3}	{[PDS]x10^2}$^{0.5}$ mol,dm^{-3}	Rp x10^5 mol.dm^{-3}.s^{-1} (without ultrasound)	Rp x 10^5 mol.dm^{-3}.s^{-1} (without ultrasound)	2 + log [PDS]	6 + log Rp (without ultrasound)	6 + log Rp (with ultrasound)
2	0.1414	0.9378	2.9072	1.3010	1.9721	2.4634
4	0.2000	1.4610	4.5144	1.6010	2.1646	2.6546
6	0.2449	1.5971	4.9191	1.7781	2.2033	2.6918
8	0.2828	1.8002	5.5266	1.9030	2.2553	2.7424
10	0.3162	2.2674	7.0062	2.0000	2.3553	2.8454
12	0.3464	2.3514	7.2893	2.0792	2.3713	2.8626

Reaction condition: [BMA], 0.2951 mol.dm^{-3}; [MPTC], 2.0 x10^{-2} mol.dm^{-3}; [H$^+$], 0.2 mol.dm^{-3}; [μ], 0.05 mol. dm^{-3}; Temp. 70°C, Time, 50 min; ultrasound condition (28 kHz, 300 W).

Table 6. Effect of various PTC on Rp

Various PTC	Rp x 10^5 mol.dm^{-3}.s^{-1} (with ultra sound)	Rp x 10^5 mol.dm^{-3}.s^{-1} (without ultrasound)
TBAI	0.4756	1.4743
TBAB	0.5028	1.5586
TBAC	0.5426	1.6820
THAC	0.5942	1.8420
MPTC	0.9378	2.9072

Reaction condition: [BMA], 0.2951 mol.dm^{-3}; [PDS], 2.0 x 10^{-2} mol.dm^{-3}; [H$^+$], 0.2 mol.dm^{-3}; [μ], 0.05 mol.dm^{-3}; Temp. 70°C, Time, 50 min; ultrasound condition (28 kHz, 300 W)

Table 7. Effect of various solvents on Rp

Solvents	Dielectric constant (ε)	Rp x 10^5 mol.dm^{-3}.s^{-1} (with ultrasound)	Rp x 10^5 mol.dm^{-3}.s^{-1} (without ultrasound)
Cyclohexanone	18.3	6.2342	2.0224
Chlorobenzene	5.8	4.8986	1.2642
Ethyl Acetate	3.88	2.9072	0.8992
Dibutyl ether	2.80	1.9645	0.7884
Toluene	2.40	1.9122	0.6898
Cyclohexane	1.14	1.2642	0.5986

Reaction condition: [BMA], 0.9378 mol.dm^{-3}; [PDS], 2.0 x10^{-2} mol.dm^{-3}; [MPTC], 2.0 x10^{-2} mol.dm^{-3}; [H$^+$], 0.2 mol.dm^{-3}; [µ], 0.05 mol.dm^{-3}; Temp. 70°C, Time, 50 min; ultrasound condition (28 kHz, 300 W).

Table 8. Effect of temperature on Rp

Temp. K	Rp x 10^5 mol.dm^{-3}.s^{-1} (without ultrasound)	Rp x 10^5 mol.dm^{-3}.s^{-1} (with ultrasound)	1/T x 10^3 K^{-1}	6 + log [Rp] (without ultrasound)	6 + log [Rp] (with ultrasound)
328	0.6464	2.0040	3.0488	1.8105	2.3018
333	0.7298	2.2477	3.0030	1.9343	2.3517
338	0.8073	2.4703	2.9585	1.9577	2.3927
343	0.9378	2.9072	2.9154	1.9721	2.4634
348	1.0678	3.3102	2.8735	1.9742	2.5198
353	1.2746	3.9257	2.8328	2.1054	2.5939

Reaction condition: [BMA], 0.9378 mol.dm^{-3}; [PDS], 2.0 x10^{-2} mol.dm^{-3}; [MPTC], 2.0 x10^{-2} mol.dm^{-3}; [H$^+$], 0.2 mol.dm^{-3}; [µ], 0.05 mol.dm^{-3}; Time, 50 min; ultrasound condition (28 kHz, 300 W).

Table 9. Thermodynamic parameter

Ea, kJ / mol	$\Delta H^{\neq}$, kJ /mol	$\Delta S^{\neq}$, eu	$\Delta G^{\neq}$, kJ /mol
47.04	44.84	-196.48	120.52

Reaction condition: [BMA], 0.9378 mol.dm^{-3}; [PDS], 2.0 x10^{-2} mol.dm^{-3}; [MPTC], 2.0 x10^{-2} mol.dm^{-3}; [H$^+$], 0.2 mol.dm^{-3}; [µ], 0.05 mol.dm^{-3}; Time, 50 min; ultrasound condition (28 kHz, 300 W).

Table 10. Effect of aqueous phase volume on Rp

V_w / V_o	$1+\log(V_w/V_o)$	Rp x 10^5 mol.dm^{-3}.s^{-1} (without ultrasonic)	Rp x 10^5 mol.dm^{-3}.s^{-1} (with ultrasonic)	5 + log [Rp] (without ultrasonic)	5 + log [Rp] (with ultrasonic)
1.00	1	0.9378	2.9072	0.9721	1.4634
0.84	0.9242	0.9046	2.7318	0.9564	1.4364
0.68	0.8325	0.8864	2.5528	0.9476	1.4070
0.52	0.7160	0.8602	2.4958	0.9345	1.3972
0.36	0.5563	0.8368	2.5140	0.9226	1.3850
0.21	0.3222	0.8016	2.3246	0.9040	1.3737

Reaction condition: [BMA], 0.9378 mol.dm^{-3}; [PDS], 2.0 x10^{-2} mol.dm^{-3}; [MPTC], 2.0 x10^{-2} mol.dm^{-3}; [H$^+$], 0.2 mol.dm^{-3}; [μ], 0.05 mol.dm^{-3}; Time, 50 min; Temp. 70°C; ultrasound condition (28 kHz, 300 W).

Figure 1: Steady State rate of Polymerization [BMA], 0.9378 mol.dm^{-3}; [PDS], 2.0 x10^{-2} mol.dm^{-3}; [MPTC], 2.0 x10^{-2} mol.dm^{-3}; [H$^+$], 0.2 mol.dm^{-3}; [μ], 0.05 mol.dm^{-3}; Temp.70°C; ultrasound condition (28 kHz, 300 W).

Figure 2: Effect of monomer concentration on Rp. [PDS], 2.0x10^{-2} mol.dm^{-3}; [MPTC], 2.0 x 10^{-2} mol.dm^{-3}; [H$^+$], 0.2 mol.dm^{-3}; [μ], 0.05 mol.dm^{-3}; Temp. 70°C, Time, 50 min; ultrasound condition (28 kHz, 300 W).

Figure 3: Effect of monomer concentration on Rp. [PDS], 2.0×10^{-2} mol.dm^{-3}; [MPTC], 2.0×10^{-2} mol.dm^{-3}; [H$^+$], 0.2 mol.dm^{-3}; [µ], 0.05 mol.dm^{-3}; Temp. 70°C, Time, 50 min; ultrasound condition (28 kHz, 300 W).
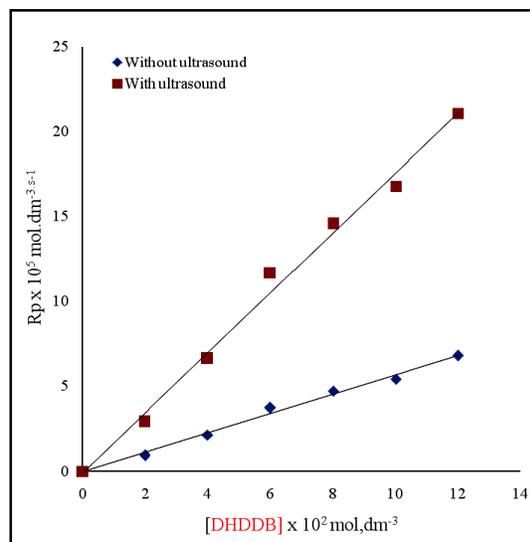

Figure 5: Effect of PTC concentration on Rp [BMA], 0.2951 mol.dm^{-3}; [PDS], 2.0×10^{-2} mol.dm^{-3}; [H$^+$], 0.2 mol.dm^{-3}; [µ], 0.05 mol.dm^{-3}; Temp. 70°C, Time, 50 min; ultrasound condition (28 kHz, 300 W).
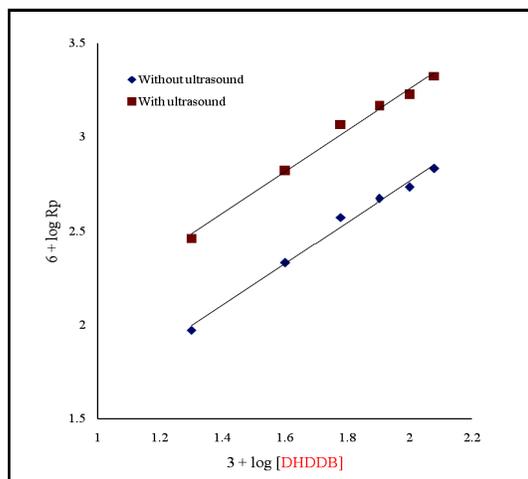
Figure 4: Effect of PTC concentration on Rp [BMA], 0.2951 mol.dm^{-3}; [PDS], 2.0×10^{-2} mol.dm^{-3}; [H$^+$], 0.2 mol.dm^{-3}; [µ], 0.05 mol.dm^{-3}; Temp. 70°C, Time, 50 min; ultrasound condition (28 kHz, 300 W).
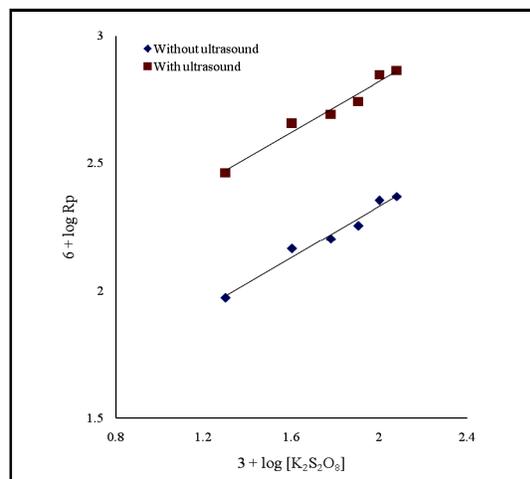
Figure 6: Effect of PDS concentration on Rp BMA], 0.2951 mol.dm^{-3}; [MPTC], 2.0×10^{-2} mol.dm^{-3}, [H$^+$], 0.2 mol.dm^{-3}; [µ], 0.05 mol. dm^{-3}; Temp. 70°C, Time, 50 min; ultrasound condition (28 kHz, 300 W).
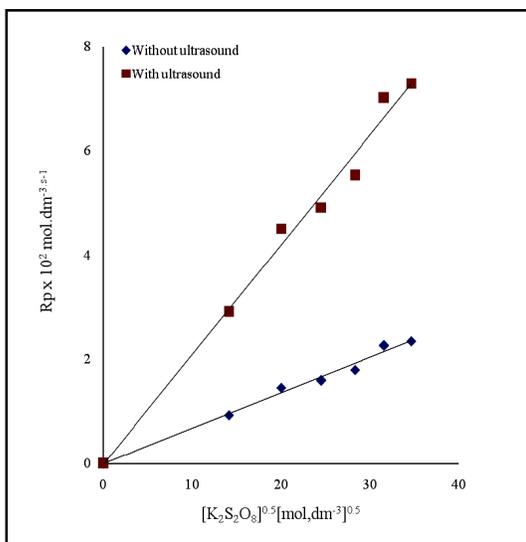
Figure 7: Effect of PDS concentration on Rp
BMA], 0.2951 mol.dm^{-3}; [MPTC], 2.0 x10^{-2}
mol.dm^{-3}, [H$^+$], 0.2 mol.dm^{-3}; [μ], 0.05 mol. dm^{-3};
Temp. 70°C, Time, 50 min; ultrasound condition
(28 kHz, 300 W).
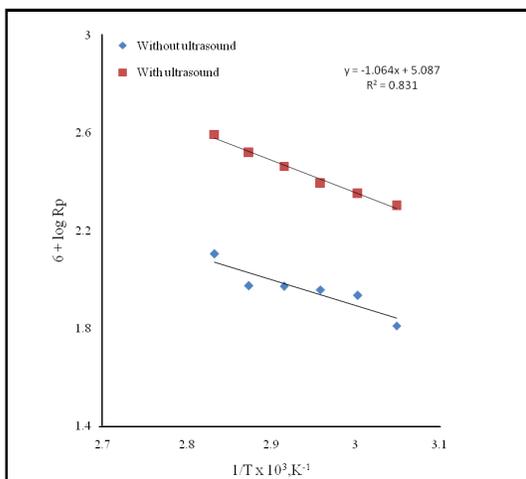
Figure 8: Effect of Temperature on Rp
[BMA], 0.9378 mol.dm^{-3}; [PDS], 2.0 x10^{-2}
mol.dm^{-3}; [MPTC], 2.0 x10^{-2} mol.dm^{-3}; [H$^+$], 0.2
mol.dm^{-3}; [μ], 0.05 mol.dm^{-3}; Time, 50 min;
ultrasound condition (28 kHz, 300 W).
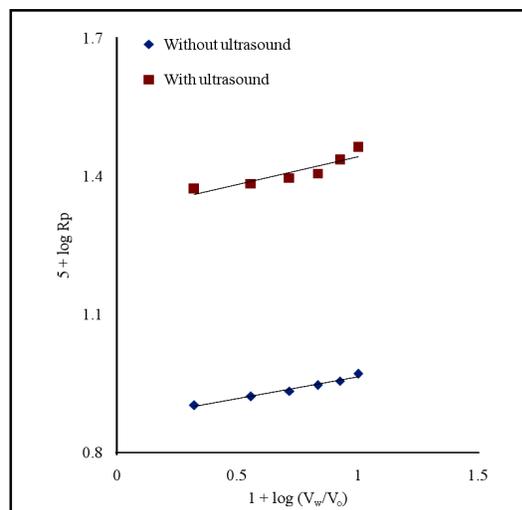
Fig. 9: Effect of aqueous phase volume on Rp
[BMA], 0.9378 mol.dm^{-3}; [PDS], 2.0 x10^{-2}
mol.dm^{-3}; [MPTC], 2.0 x10^{-2} mol.dm^{-3}; [H$^+$], 0.2
mol.dm^{-3}; [μ], 0.05 mol.dm^{-3}; Time, 50 min; Temp.
70°C; ultrasound condition (28 kHz, 300 W).

3.8 Effect of temperature on Rp :

The polymerization was carried out at
different temperatures, $i.e.$, from 328 to353, K
at definite concentrations of BMA, $K_2S_2O_8$, MPTC,
H$^+$ and ionic strength. The rate of polymerisation
increases with temperature [Table 8]. The
activation energy for the overall rate of polyme-
risation has been computed from the Arehenius
plot of log Rp vs 1/T [Fig. 8] and it was found
to be 47.04, kJ.mol^{-1}. the other thermodynamic
parameters such as $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ have
also been calculated from the Eyring plot of
log Rp/T vs 1/T and are presented in Table 9.

3.9 Effect of volume fraction of aqueous on Rp :

The effect of variation in the ratio of
volume of aqueous phase (Vw) to volume of

organic phase (Vo), Vw/Vo, on the Rp was studied in the range of 0.21 – 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 Rp with an increase in volume fraction of aqueous phase ratio (Vw). From the slope of linear plot of 5+ log Rp vs 1+ log (Vw/Vo) the reaction order with respect to (Vw/Vo) was found to be 0.12 (Table 10, Fig. 9). Balakrishnan et al observed the reaction exponents with respect to Vw/Vo in the polymerisation 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)[29]. However, Simionescu and coworkers reported an independent nature of Rp on Vw/Vo in the polymerization of MMA using $K_2S_2O_8$– Arquad phase-transfer catalyst system[30].

3.10 Effect of acid [H^+] and ionic strength (μ) on Rp :

The effect of acid and ionic strength on the rate of polymerization was studied by varying [H^+] and μ, *i.e.*, [K_2SO_4], independently at definite concentrations monomer, initiator and PTC. Variation in either [H^+] or μ of the medium have no discernible effect on Rp.

4. Mechanism and rate law :

A mechanism has been proposed to explain the above mentioned experimental observations.

Phase Transfer

$$2Q^+ + S_2O_8^{2-} \leftrightarrow Q_2S_2O_8 \qquad (1)$$
(W)   (W)   (O)

Initiation

$$Q_2S_2O_8 \xrightarrow{k_d} 2Q^+ + 2SO_4^{•-} \qquad (2)$$
(o)

$$SO_4^{•-} + M_{(o)} \xrightarrow{k_i} \dot{M}_1 \qquad (3)$$
(o)   (BMA)

Propagation

$$\dot{M}_1 + M \xrightarrow{k_p} \dot{M}_2$$

$$\cdots\cdots\cdots$$
$$\cdots\cdots\cdots \qquad (4)$$
$$\cdots\cdots\cdots$$

$$\dot{M}_{n-1} + M \longrightarrow \dot{M}_n \qquad (5)$$
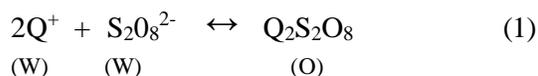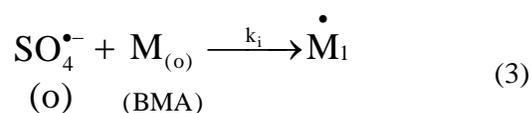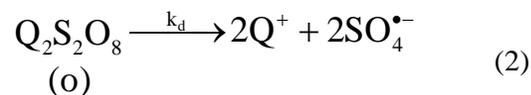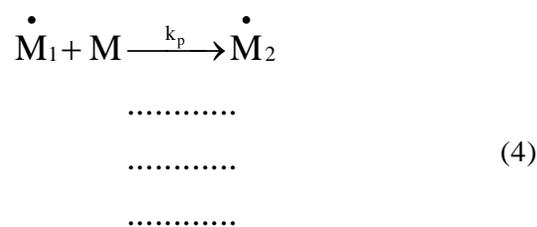
The termination occurs by the combination of two growing polymer chain radicals, it can be represented as

$$2\dot{M}_n \xrightarrow{k_t} polymer \qquad (6)$$
(Poly benzyl methacrylate)
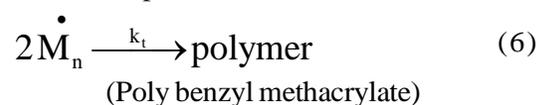
Where K is equilibrium constant, k_d is the reaction rate constant of decomposition, k_i is the reaction initiation rate constant, k_p is the propagation rate constant and k_t is the reaction rate constant of termination. The subscripts (o) and (w) refer to organic phase and aqueous phase respectively. Q^+ refers to the cation of phase-transfer catalyst. This mechanism involves the formation of quaternary ammonium peroxydisulfate complex ($Q_2S_2O_8$) in the aqueous phase, which is then transferred to the organic phase. The decomposition of $Q_2S_2O_8$ takes place in the organic phase leading to the formation of $2Q^+SO_4^{•-}$.

Applying the general aspects of 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

$$R_i = k_i[M][SO_4^{\bullet -}] \tag{7}$$

$$R_i = \frac{-d\lfloor SO_4^{\bullet -} \rfloor}{dt} = 2k_d K [Q^+]_w^2 [S_2O_8^{2-}]_w \tag{8}$$

The rate of propagation is given by

$$R_p = k_p [\overset{\bullet}{M}][M] \tag{9}$$

$$[\overset{\bullet}{M}] = \frac{R_p}{k_p[M]} \tag{10}$$

The rate of termination (R_t) is given by

$$R_t = 2k_t [\overset{\bullet}{M}]^2 \tag{11}$$

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

$$R_i = R_t \tag{12}$$

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

$$[\overset{\bullet}{M}]^2 = \frac{k_d K [Q^+]_w^2 [S_2O_8^{2-}]_w}{k_t} \tag{14}$$

$$[\overset{\bullet}{M}] = \left[\frac{k_d K_w}{k_t}\right]^{\frac{1}{2}} [Q^+]_w [\ S_2O_8^{2-}]^{1/2} \tag{15}$$

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

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

The above equation satisfactorily explains all the experimental observations.

Conclusion

In this study, the radical polymerization of benzyl methacrylate by ultrasound assisted phase-transfer catalysis in ethyl acetate/water biphasic system at $70 \pm 1\,^oC$ under inert atmosphere is reported. The parameters influencing the rate of polymerization were performed with/without ultrasound irradiation. It shows that the Rp enhanced almost three fold and eight fold with 28 kHz (300W) and 40 kHz (300W) under ultrasound irradiation condition compared with the conduct of the same polymerization without ultrasound irradiation. The Rp value increases with increasing the [BMA], [K$_2$S$_2$O$_8$], [MPTC] and temperature. From the Arrhenius plot the energy of activation E$_a$, and other thermodynamic parameters such as entropy of activation ($\Delta S^{\#}$), enthalpy of activation ($\Delta H^{\#}$) and free energy of activation ($\Delta G^{\#}$) have been calculated. Based on the kinetic results, a suitable mechanism has been proposed.

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