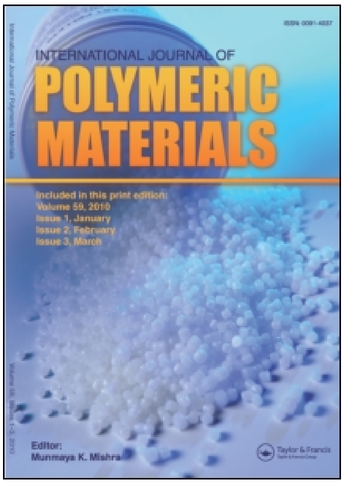

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Synthesis, Characterization and Application of a Multi-Site Phase Transfer Catalyst in Radical Polymerization of n-Butyl Methacrylate—A Kinetic Study

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The multi-site phase transfer catalyzed radical polymerization of n-butyl methacrylate (n-BMA) using newly synthesized and characterized 1,1,2,2-tetramethyl-1-benzyl-2-n-propylethylene-1,2-diammonium bromide chloride (TMBPEDBC) as a multi-site phase transfer catalyst was investigated in an aqueous-organic two-phase system at $60 \pm 1^{\circ}C$ under nitrogen circumstances. The kinetics and effects of various operating variables (monomer, initiator, catalyst, temperature, acid, and ionic strength) on the rate of polymerization (Rp) were examined in detail. The order with respect to monomer, initiator and multi-site phase transfer catalyst was found to be 0.50. A suitable kinetic reaction scheme has been proposed to account for experimental observations, and its significance is discussed.

Keywords kinetics, multi-site phase transfer catalyst (MPTC), radical polymerization, rate of polymerization (Rp)

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INTRODUCTION

Phase transfer catalysis (PTC) is a very useful technique to promote the reaction between two mutually insoluble phases that typically involves simple experimental procedures, mild reaction conditions, inexpensive and eco-friendly reagents and solvents, and is suitable for large-scale reactions [1]. The most essential consideration in phase transfer catalyzed reactions is that the catalyst must have the ability to transfer the reacting anions into the other phase to react with the substrates. In a liquid-liquid system, the aqueous nucleophile reacts with the catalyst to form an ion-pair, which transfers into the organic phase to conduct the reaction. The catalyst is then regenerated and transfers back to the aqueous phase to conduct the next cycle of reaction. Generally quaternary ammonium and phosphonium salts, crown ethers, poly(ethylene glycol)s and cryptates are often used as the phase transfer catalysts [2,3].

The kinetics of radical polymerization of vinyl monomers assisted by phase transfer catalysts (PTC) is a field that has attracted significant interest in the recent past. The use of different commercially available single-site PTC (quaternary ammonium salts) aided free radical polymerization of hydrophobic vinyl monomers using peroxo salts as initiators has been reported [4–10].

The synthesis and application of multi-site phase transfer catalyst (MPTC) has gained remarkable interest because of the multi-site type of onium salts, which have facile synthesis, low energy consumption and high reactivity in particular reactions under mild experimental conditions compared to commercially available onium salts. Recently, we have reported multi-site phase transfer catalyzed radical polymerization of acrylonitrile (AN) [11,12], methyl methacrylate (MMA) [13], ethyl methacrylate (EMA) [14] and glycidyl methacrylate (GMA) [15] in an aqueous-organic two-phase system. Consecutively, we have undertaken an effort to work on synthesis, characterization of multi-site phase transfer catalyst (TMBPEDBC) and application in kinetics of radical polymerization of n-butyl methacrylate (n-BMA) using potassium peroxy disulfate (PDS) as a water-soluble initiator in a cyclohexane/water two-phase system.

EXPERIMENTAL

Materials

N-butyl methacrylate (Lancaster, Chennai, India), N,N,N′,N′-tetramethylethylenediamine (Lancaster, Chennai, India), n-propyl bromide, benzyl chloride (SRL, Mumbai, India), potassium peroxydisulfate (PDS) (Merck, Mumbai, India), and methanol (SRL, Mumbai, India) were used as received. The distilled water and cyclohexane were used as a solvent for the two-phase system.

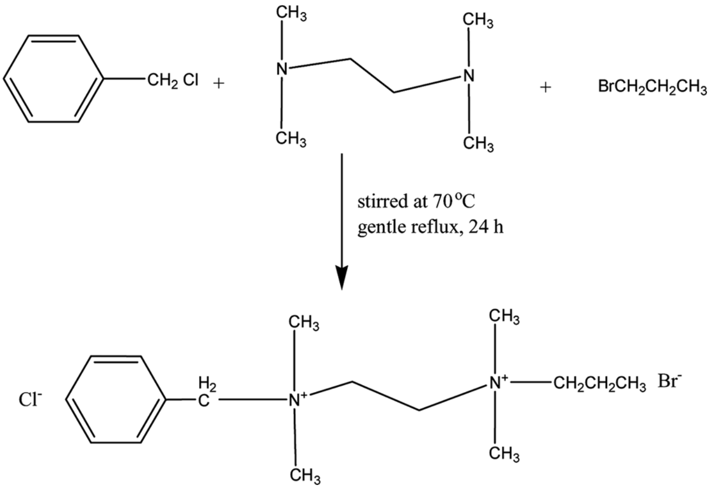
The multi-site phase transfer catalyst, 1,1,2,2-tetramethyl-1-benzyl-2-n-propylethylene-1,2-diammonium bromide chloride (TMBPEDBC) was synthesized by the following procedure.

Synthesis of Multi-Site Phase Transfer Catalyst (TMBPEDBC)

N,N,N′,N′-tetramethylethylenediamine (0.01 mol) was dissolved in ethanol (approximately 10 ml), placed in a two-necked round-bottom flask, and stirred at 70°C. The n-propyl bromide (0.01 mol dissolved in ethanol) was added drop-wise. After one hour, a solution of benzyl chloride (0.01 mol dissolved in ethanol) was slowly added to the reaction mixture. The reaction mixture was gently refluxed and stirred for 24 h. After that, the mixture was cooled to room temperature and the solvent was evaporated. The white precipitate of 1,1,2,2-tetramethyl-1-benzyl-2-n-propylethylene-1,2-diammonium bromide chloride (TMBPEDBC) was obtained. It was purified by dissolving a minimum amount of catalyst in ethanol and diffusing over hexane; pure white precipitate was collected and dried. The melting point of the catalyst was 210°C (Scheme 1).

Instruments

The viscosity average molecular weight (M_v) of the polymer was determined in butanone at 30 ± 1°C with the help of an Ubbelohde viscometer using the Mark-Houwink equation. From the molecular weight of the polymer, the degree of polymerization was calculated. The FTIR spectrum of the catalyst



Scheme 1: Synthesis of multi-site phase transfer catalyst (TMBPEDBC).

was recorded on a FTIR spectrometer (Perkin Elmer RX I) in the spectral region from 4000 to 500 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian 100 HA JEOL 400 MHz spectrometer by using D_2O as a solvent and tetramethylsilane as an internal reference.

Characterization of Multi-Site Phase Transfer Catalyst

FTIR Spectroscopy

FTIR (KBr, cm^{-1}): 1356 (methyl), 1466 (methylene), 1214 (-C-N stretching), 1480 and 1618 (aromatic ring), 2368 (aliphatic -C-H stretching), 900–690 (aromatic -C-H out of plane bending vibrations) and 690 (mono substituted ring stretching) (Figure 1).

^{1}HNMR Spectroscopy

^{1}HNMR: (400 MHz, D_2O) δ ppm = 1.0 (t, 3H, methyl), 1.17 (q, 4H, methylene), 3.0 (t, 12H, $-N-CH_3$), 3.3–3.5 (m, 4H, $-N-CH_2$), 4.20 (s, 2H, benzyl) and 7–8 (s, 5H, aromatic) (Figure 2).

^{13}CNMR Spectroscopy

^{13}CNMR (400 MHz, D_2O): δ ppm = 12.60 (methyl carbon), 15.30 (methylene carbon), 66.7–68.0 (methylene carbon of $-N-CH_2$ group), 52.2–58.7 (methyl carbon of $-N-CH_3$ group) and 129–135 (aromatic ring carbon) (Figure 3).

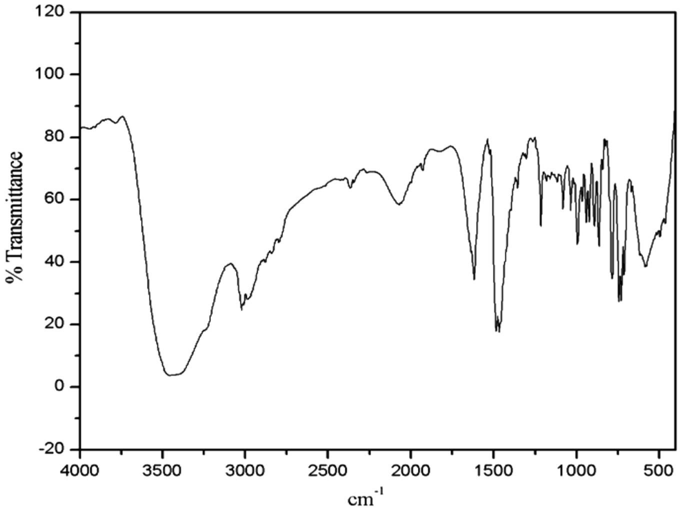


Figure 1: FTIR spectral analysis of 1,1,2,2-tetramethyl-1-benzyl-2-n-propylethylene-1,2-diammonium bromide chloride.

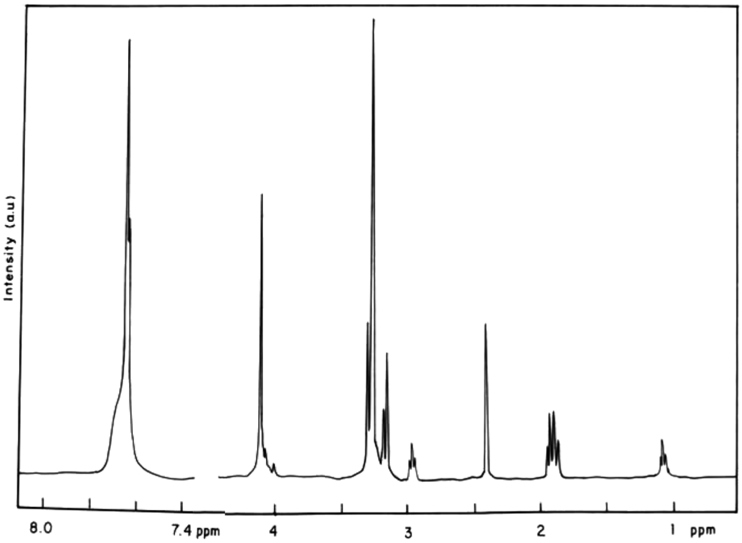


Figure 2: ^{1}HNMR spectral analysis of 1,1,2,2-tetramethyl-1-benzyl-2-n-propylethylene-1,2-diammonium bromide chloride.

Polymerization of n-BMA

The polymerization reaction tube consists of equal volumes of aqueous phase and organic phase (10 ml each). The reaction mixture was thoroughly deaerated for 30 min. After, the reaction tube was placed in the temperature water bath at temperature (60 ± 1°C) under unstirred conditions. A known

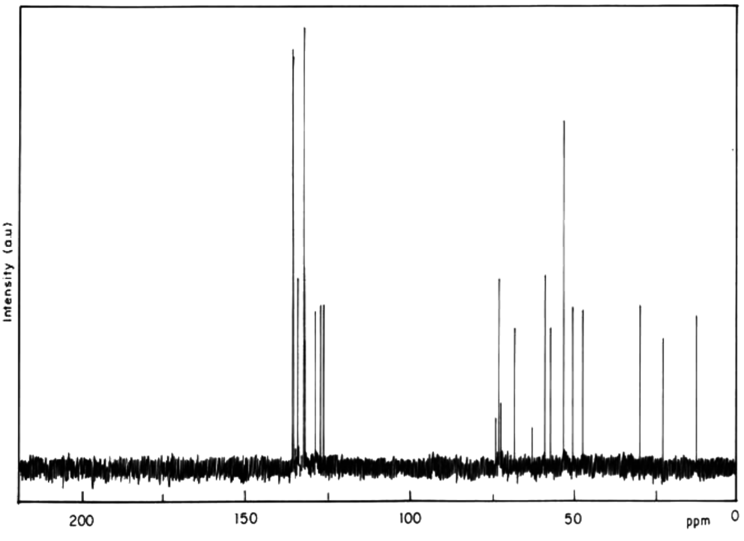


Figure 3: ^{13}C-NMR spectral analysis of 1,1,2,2-tetramethyl-1-benzyl-2-n-propylethylene-1,2-diammonium bromide chloride.

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

$$\mathrm{Rp} = 1000\,\mathrm{W/VtM}$$

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

RESULTS AND DISCUSSION

Steady State Rate of Polymerization

The steady state rate of polymerization for the n-butyl methacrylate was studied by determining Rp at different intervals of time. The plot of Rp vs. time shows an increase to some extent, decreased thereafter and then reached the constant value of Rp. The steady state rate of polymerization reaction time was fixed at 40 min to carry out the experiments with different reaction conditions (Figure 4).

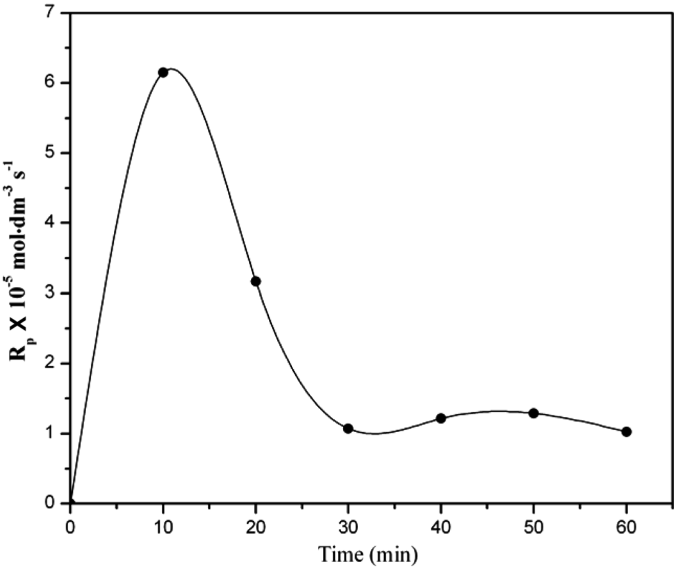


Figure 4: Steady state rate of polymerization. Polymerization condition: (n-BMA): 2.0 mol dm^{-3}; ($K_2S_2O_8$): 2.0 × 10^{-2} mol dm^{-3}; (TMBPEDBC): 2.0 × 10^{-2} mol dm^{-3} (H^+): 0.5 mol dm^{-3}; (μ): 0.2 mol dm^{-3}; Temperature: 60 ± 1°C.

Effect of Varying Monomer Concentration

The effect of monomer concentration on the rate of polymerization (Rp) was varied from 4.5 to 9.5 mol dm^{-3} by keeping the concentration of PDS, MPTC, acid and ionic strength constant. Rp increases with an increasing concentration of n-BMA due to the accessibility of monomer molecules in the propagation step increases, which obviously increases the rate of polymerization. The reaction order with respect to [n-BMA] was calculated from the plot of (6 + log Rp) vs. (3 + log[n-BMA]) and it was found to be 0.50. A plot of Rp vs. [n-BMA] passing through the origin confirms the above observations (Figure 5). At higher monomer concentration, the rate of polymerization (Rp) reaches the constant value. This may be attributed to an increase in the viscosity of the medium and difficult diffusion of the ions through the medium.

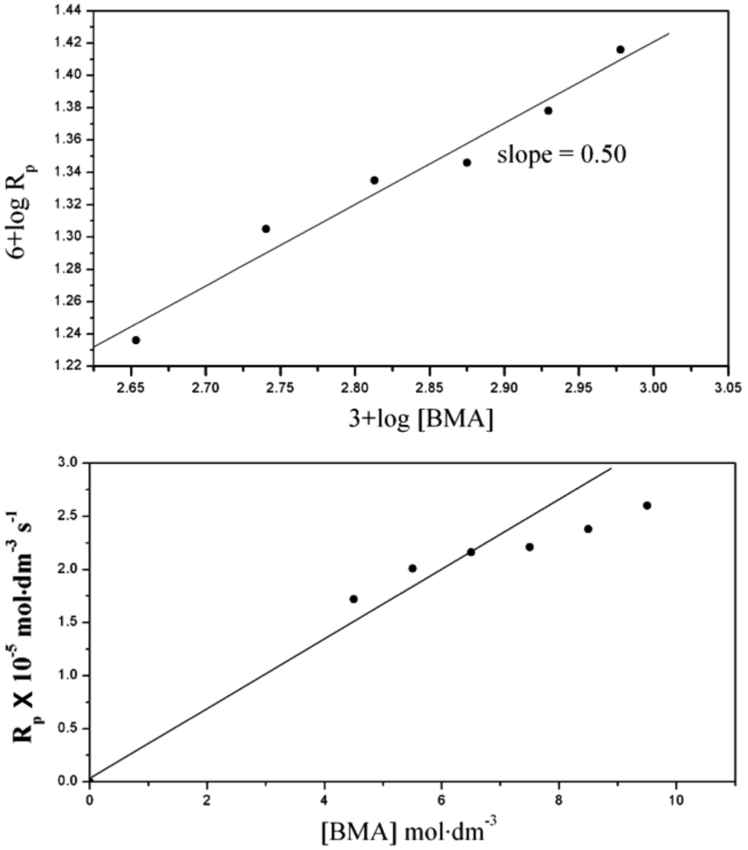


Figure 5: Effect of varying monomer concentration. Polymerization condition: ($K_2S_2O_8$): 2.0×10^{-2} mol dm^{-3}; (TMBPEDBC): 2.0×10^{-2} mol dm^{-3}; (H^+): 0.5 mol dm^{-3}; (μ): 0.2 mol dm^{-3}; Temperature: 60 ± 1°C.

Effect of Varying Initiator Concentration

The effect of initiator concentration on the rate of polymerization (Rp) was studied by varying the concentration in the range of 1.5 to 2.5 mol dm^{-3} at fixed reaction conditions. An increase in the rate of polymerization (Rp) occurs with an increase in initiator concentration. This is attributed to an increased concentration of active radical species in the organic phase. The order of the reaction with respect to the initiator was found to be 0.58 by plotting $(6 + \log \mathrm{Rp})$ vs. $(3 + \log[K_2S_2O_8])$. The Rp vs. $[K_2S_2O_8]$ is linear, passing through the origin supporting the above deduction (Figure 6).

Effect of Varying Catalyst Concentration

The effect of concentration of a multi-site phase transfer catalyst, 1,1,2,2-tetramethyl-1-benzyl-2-n-propylethylene-1,2-diammonium bromide chloride (TMBPEDBC), on the rate of polymerization was studied by varying concentration in the range 1.5 to 2.5 mol · dm^{-3} at a fixed reaction condition. Rp increases with an increase in concentration of multi-site PTC. Generally, the

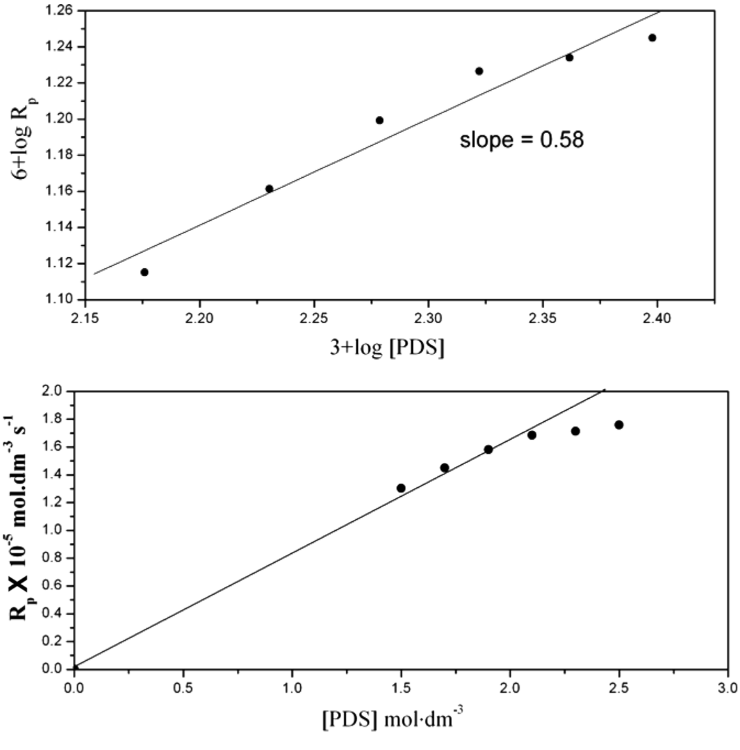


Figure 6: Effect of varying initiator concentration. Polymerization condition: (n-BMA): 2.0 mol dm^{-3}; (TMBPEDBC): 2.0×10^{-2} mol dm^{-3}; (H^+): 0.5 mol dm^{-3}; (μ): 0.2 mol dm^{-3}; Temperature: 60 ± 1°C.

efficiency of a phase transfer catalyst depends on the influence of cation, anion, and organic solvents. From the observed results, the rate of polymerization (Rp) increases with an increase in concentration of catalyst due to a number of active sites and the high lipophilic character of the catalyst.

The order of the reaction was obtained from the plot of (6 + log Rp) vs. (3 + log[TMBPEDBC]). It was found to be 0.52. The plot of Rp vs. [TMBPEDBC] passing through the origin confirms the above observations (Figure 7). The half order with respect to the catalyst has already been reported in the phase transfer catalyst-assisted polymerization of vinyl monomers [11–15]. In the absence of a multi-site phase transfer catalyst, no polymerization reaction occurred which confirmed the role of multi-site PTC in the reaction.

Effect of Varying Temperature

The effect of varying temperature on the rate of polymerization (Rp) was studied in the temperature range 323–333 K by keeping other variables constant. The rate of polymerization increases with an increase in temperature. The increase in the rate of polymerization with increasing temperature is

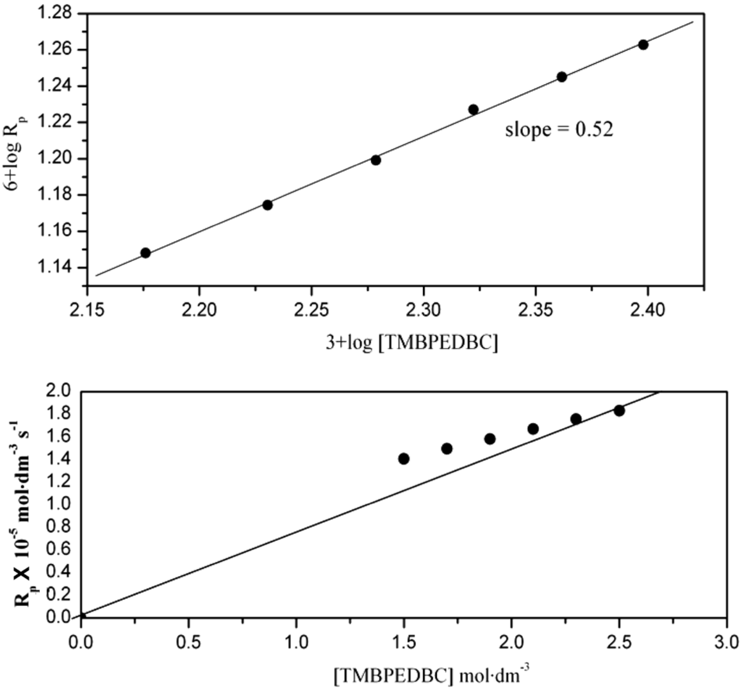


Figure 7: Effect of varying catalyst concentration. Polymerization condition: (n-BMA): 2.0 mol dm^{-3}; ($K_2S_2O_8$): 2.0 × 10^{-2} mol dm^{-3}; (H^+): 0.5 mol dm^{-3}; (μ): 0.2 mol dm^{-3}; Temperature: 60 ± 1°C.

Table 1: Activation parameter.

Ea kJ/mol	$\Delta G^{\#}$ kJ/mol	$\Delta H^{\#}$ kJ/mol	$\Delta S^{\#}$ kJ/mol
3.86	103.4	63.37	−120.26

due to an increase in the decomposition of the initiator in the organic phase and transportation of the initiator from the aqueous phase to organic phase also accelerated at high temperature, which lead to an increase in the rate of polymerization. The activation energy (Ea) and other activation parameters such as entropy of activation ($\Delta S^{\#}$), enthalpy of activation ($\Delta H^{\#}$) and free energy of activation ($\Delta G^{\#}$) have been calculated from the plot of $6 + \log Rp$ vs. 1/T (Table 1, Figure 8).

Effect of Varying Volume Fraction of Aqueous Phase

The effect of volume fraction of the aqueous phase on the rate of polymerization (Rp) was studied by varying the fraction of the aqueous phase in the range (V_w/V_o) 0.29–0.90) at fixed concentrations of all other parameters. There is no significant change in the rate of polymerization observed with an increase in volume fraction of aqueous phase. From the plot of ($6 + \log Rp$) vs. $1 + \log(V_w/V_o)$ in Figure 9, the reaction order with respect to (V_w/V_o) was found to be 0.068.

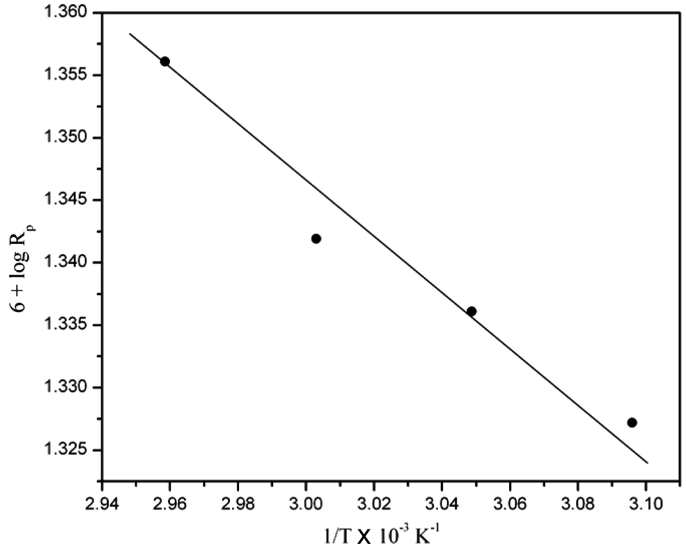


Figure 8: Effect of varying temperature. Polymerization condition: (n-BMA): 2.0 mol dm^{-3}; ($K_2S_2O_8$): 2.0×10^{-2} mol dm^{-3}; (TMBPEDBC) : 2.0×10^{-2} mol dm^{-3} (H^+): 0.5 mol dm^{-3}; (μ): 0.2 mol dm^{-3}.

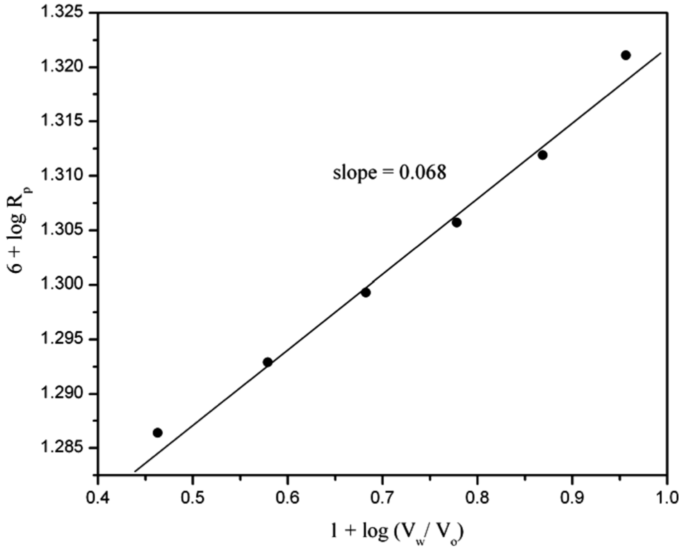


Figure 9: Effect of varying volume fraction of aqueous phase. Polymerization condition: (n-BMA): 2.0 mol dm^{-3}; ($K_2S_2O_8$): 2.0 × 10^{-2} mol dm^{-3} ; (TMBPEDBC): 2.0 × 10^{-2} mol dm^{-3} (H^+): 0.5 mol dm^{-3}; (μ): 0.2 mol dm^{-3}; Temperature: 60 ± 1°C.

Effect of Varying Acid (H^+) and Ionic Strength (μ)

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

Effect of Varying Water Immiscible Organic Solvents

The effect of water-immiscible organic solvents on Rp was examined by using three different immiscible organic solvents such as cyclohexanone, ethyl acetate and cyclohexane. The rate of polymerization increases with an increase in polarity of solvents. This could be explained by the fact that these solvents have high dielectric constants and polarity, which facilitates to increase the transfer of peroxydisulfate from the aqueous phase to organic phase. The rate of polymerization (Rp) decreases in the following order: cyclohexanone > ethyl acetate > cyclohexane (Table 2).

Reaction Scheme and Mechanism

Scheme 2 represents the reactions characterizing the polymerization of n-butyl methacrylate (M) initiated by $K_2S_2O_8$/MPTC in cyclohexane/water two-phase systems. It is assumed that dissociation of QXY and $K_2S_2O_8$, formation of QS_2O_8 in the aqueous phase, and initiation of the monomer in the organic phase, occurs along the reactions such as Eqs. (1)–(5). The equilibrium

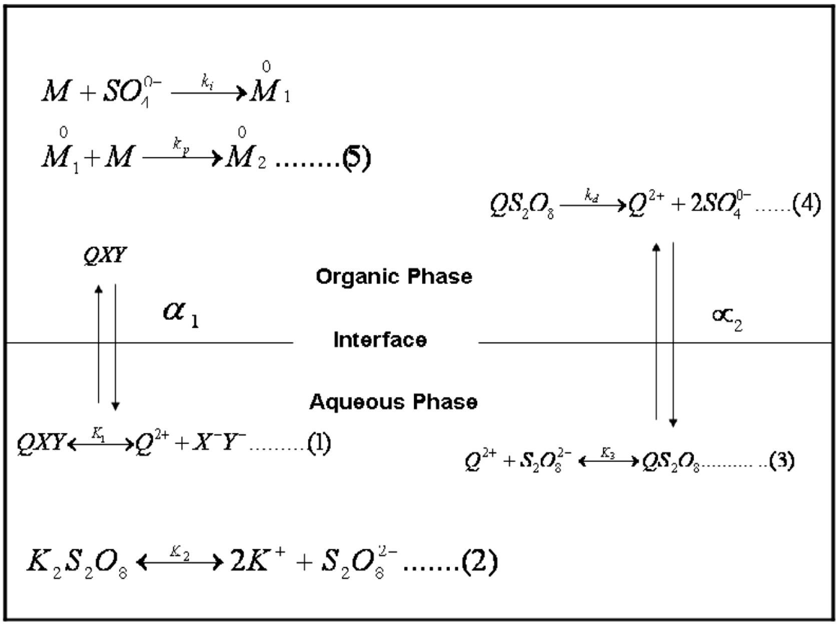
Table 2: Effect of water-immiscible organic solvents.

	Rp × 10^5 mol dm^{-3} s^{-1}		
Reaction conditions	**Cyclohexanone (18.3)**	**Ethyl acetate (3.91)**	**Cyclohexane (1.13)**
(n-BMA): 2.0 mol dm^{-3}; ($K_2S_2O_8$): 2.0 × 10^{-2} mol dm^{-3}; (TMBPEDBC): 2.0 × 10^{-2} mol dm^{-3}; (H^+): 0.5 mol dm^{-3}; (μ): 0.2 mol dm^{-3}; Temperature: 60 ± 1°C	2.95	2.04	1.98

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

$$K_1 = \frac{[Q^{2+}]_w[XY]_w}{[QXY]_w} \tag{6}$$

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



Scheme 2: Polymerization using multi-site phase transfer catalyst (MPTC) in an aqueous-organic two-phase system.

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

$$\alpha_1 = \frac{[Q^{2+}XY]_w}{[QXY]_o} \tag{9}$$

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

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

$$R_i = \frac{d[SO_4^{\bullet -}]}{dt} = 2K_d f K_3[Q^{2+}]_w[S_2O_8^{2-}]_w \tag{11}$$

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

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

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

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

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

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

The termination occurs by the combination of two growing polymer chain radicals, and can be represented as:

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

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

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

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

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

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

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

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

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

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

The above equation satisfactorily explains all the experimental observations. The rate of polymerization (Rp) increases with an increase in concentrations of n-BMA, PDS, and multi-site phase transfer catalyst. The expression for the degree of polymerization was represented as follows:

$$\overline{P_n} = \frac{R_p}{R_t} \tag{23}$$

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

The degree of polymerization $\overline{P_n}$ is directionally proportional to [M]. It was found that the plot of $\overline{P_n}$ versus [M] gives a straight line passing through the origin for n-butyl methacrylate system (Figure 10). This observation supports the derived mechanism.

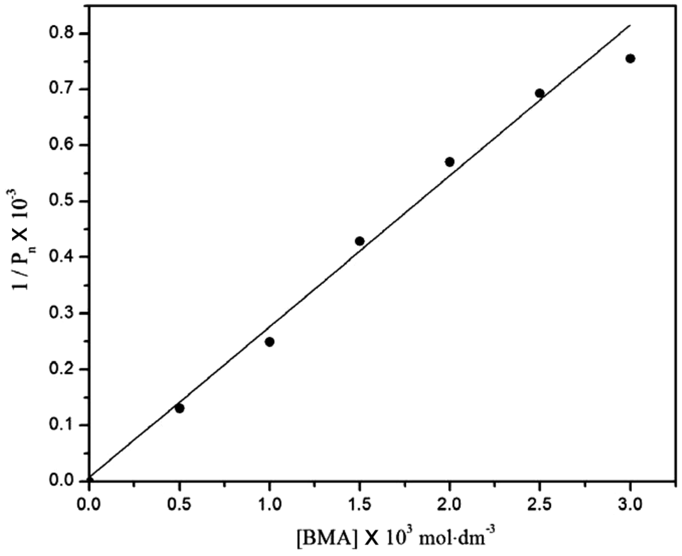


Figure 10: n-BMA- TMBPEDBC -$K_2S_2O_8$ system dependence of $\overline{P_n}$ on (n-BMA).

CONCLUSIONS

The n-butyl methacrylate was successfully polymerized by using newly synthesized and characterized 1,1,2,2-tetramethyl-1-benzyl-2-n-propylethylene-1,2-diammonium bromide chloride (TMBPEDBC) as a multi-site phase transfer catalyst together with potassium peroxydisulfate (water-soluble initiator) in a cyclohexane/water two-phase system at $60 \pm 1°C$ under inert atmosphere via free radical mechanism. The polymerization reaction order with respect to monomer, initiator and catalyst was found to be 0.50. The rate of polymerization increases with an increase in temperature and the polarity of water-immiscible organic solvents. The acid and ionic strength of the medium does not show any appreciable effect on the Rp. On the basis of the obtained results a suitable kinetic reaction scheme and mechanism has been proposed.

SYMBOLS AND ABBREVIATIONS

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

Greek Letters

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

Subscripts

o	Organic phase
w	Aqueous phase

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