

Free Radical Polymerization of Methyl and Ethyl Methacrylates by Green Methodology

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Abstract

The efficiency of newly synthesized single site phase transfer catalyst has been studied with the help of kinetics of free radical polymerization of methyl and ethyl methacrylate (MMA and EMA). The radical polymerization was catalyzed with single site phase transfer catalyst, 2-benzoyldecyldimethylammonium bromide (BEDDAB) and initiated by water soluble potassium peroxydisulphate initiator in ethyl acetate / water biphasic media under inert condition at constant temperature $60 \pm 1^\circ\text{C}$. The prepared phase transfer catalyst has been characterized by FT-IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ as well as C, H and N elemental analysis. The order of the reaction with respect to monomer, initiator, phase transfer catalyst (PTC) and temperature was ascertained. A suitable kinetic mechanism has been proposed as per the experimental conditions. Molecular weight of the polymethyl methacrylate (PMMA) as well as polyethylmethacrylate (PEMA) which have been polymerized using phase transfer catalyst was evaluated using GPC technique.

Keywords: Single site phase transfer catalyst; 2-Benzoyldecyldimethylammonium bromide; Kinetic mechanism; Radical polymerization.

Introduction

Rapid industrialization and revolution has focused significant attention on green chemistry. Among the new developments in the organic synthesis towards green technology, reactions involving phase transfer catalyst has become a versatile technique because of its *mild reaction conditions, large conversion and product selectivity* [1-3]. Though the reaction between hydrophilic and lipophilic reactants can be facilitated by appropriate aprotic solvent, the separation of solvent from the reaction mixture and the cost has established the phase transfer catalyst as a power tool in bringing plausible reaction between two mutually immiscible phases. The first published biphasic method for the generation of dichlorocarbene by Makosza [4] has triggered and propelled the application of phase transfer catalyst in organic synthesis. Hence it has become a fascinating area of research. Researchers studied the

success of single site phase transfer catalyst especially in free radical vinyl monomers involving aqueous-organic biphasic media [5-17]. These studies provoked us to check the efficiency of a newly synthesized single-site phase transfer catalyst by polymerizing MMA and EMA and its competency has been analyzed by kinetic study using water soluble potassium peroxydisulphate (PDS) initiator.

Experimental Details

Materials and Methods

The monomers methyl methacrylate and ethyl methacrylate (Merck, Mumbai) were subjected to reduced pressure distillation before use. The water soluble initiator, potassium peroxydisulphate (SRL, Mumbai) was used as such. Methanol (SRL, Mumbai) was distilled over a water bath and used. Formaldehyde (SRL Mumbai) was used as received. Dimethyl amine (Merck) acetophenone (Merck) ethyl acetate (SRL, Mumbai) were distilled before use. Double distilled water was used as solvent for the biphasic system.

Instrumentation

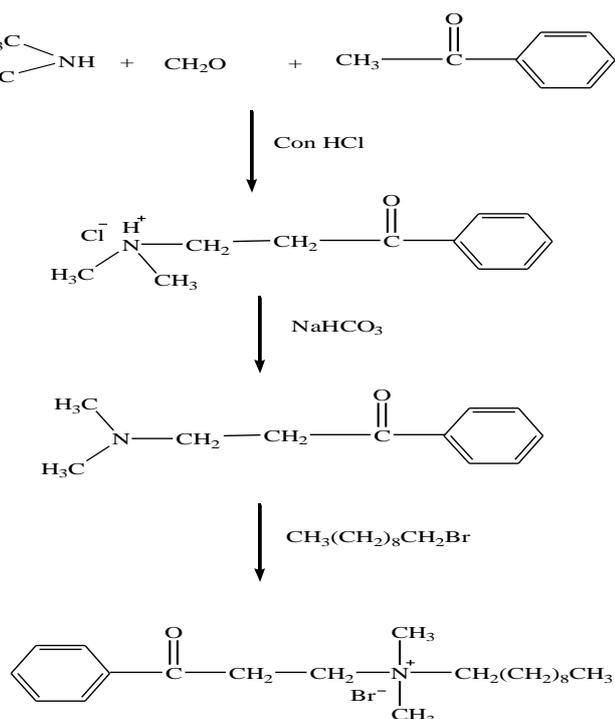
The FT-IR spectrum was recorded on a Perkin Elmer RX I spectrometer in the spectral region from 4400 to 400 cm^{-1} using KBr. High resolution $^1\text{H-NMR}$ spectra and $^{13}\text{C-NMR}$ spectra was recorded on a Bruker 500 MHz and Bruker DRX 125.77 MHz FT-NMR spectrometers at room temperature using D_2O solvent. Molecular weight of the polymer was determined by Waters 501 gel permeation chromatograph. Tetrahydrofuran was used as an eluent and polystyrene standards were employed for calibration. The glass transition temperature was determined with a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of $10^\circ\text{C}/\text{min}$ in N_2 atmosphere.

Synthesis of 2-Benzoyldecyldimethylammonium bromide (BEDDAB)

Single site phase transfer catalyst was prepared in two stages. In the first stage dimethylamine propiophenone hydrochloride was prepared as reported in the literature [18] by treating equal moles (0.33 mole) of dry methylamine, powdered para

formaldehyde and acetophenone and 40 ml of 95% ethanol containing 0.5 ml of conc. HCl.

In the second stage 0.28 mole of the prepared dimethylaminepropiofenone hydrochloride was taken in a separating funnel and mixed with ether. Then 100 ml of sodium bicarbonate (0.1N) solution was added little by little and the separation funnel was shaken from time to time. The free amine, dimethylaminepropiofenone was extracted in ether. The ether layer containing the amine was quaternized by the addition of 0.28 mole of n-bromodecane in cold conditions. The product was allowed to stand overnight in a closed vessel and then filtered. The obtained product was purified by recrystallization using acetone-alcohol mixture. After being dried in a vacuum at 60°C for 24 hrs, the purified 2-benzoyldecyldimethylammonium bromide (BEDDAB) was collected. The yield in the second stage was 90%. The synthesis of BEDDAB is shown in Scheme 1



Scheme 1. Synthesis of Benzoyldecyldimethylammonium bromide

Polymerization Procedure

A typical polymerization of the monomers, methyl methacrylate (MMA) and ethylmethacrylate (EMA) was carried out using a long closed Pyrex tube under unstirred, inert atmospheric conditions at 60±1°C. The reaction mixture consists of monomer in 10 ml organic phase (ethyl acetate) and the phase transfer catalyst (BEDDAB), sodium bisulphate (0.5 mole dm⁻³) for adjusting the ionic strength and sulphuric acid (0.2 mol dm⁻³) for maintaining the pH in 10 ml of aqueous phase.

Polymerization reaction was initiated by the addition of potassium peroxydisulphate (PDS) to the reaction mixture. After stipulated time, the reaction was arrested by pouring the

reaction mixture into ice cold methanol [5-9, 12, 13, 17]. The precipitated polymer was filtered through a sintered glass crucible, washed with double distilled water and methanol and then dried in oven (60 ± 0.1°C) until constant weight was obtained. The rate of polymerization (Rp) was calculated using equation (1).

$$R_p = \frac{1000 \times W}{V \times t \times M} \quad \text{--- (1)}$$

Where Rp-Rate of Polymerization; W-Weight of polymer in grams, V-Volume of reaction mixture; t-Reaction time in seconds; M-Molecular weight of the monomer.

Results and Discussion

Synthesis of 2-Benzoyldecyldimethylammonium bromide (BEDDAB)

In the first stage dimethylaminepropiofenone hydrochloride was prepared by condensing dimethylamine and acetophenone with formaldehyde in the presence of conc.HCl at slightly warm conditions.

The dimethylaminepropiofenone hydrochloride was then neutralized by treating with sodium bicarbonate to isolate dimethylaminepropiofenone which was extracted with ether. The amine was then quaternized by the addition of n-bromodecane in cold conditions. Thus the obtained product was purified by recrystallization using acetone-alcohol mixture. After being dried in a vacuum at 60°C for 24 hrs, the purified 2-benzoyldecyldimethylammonium bromide was collected. The synthesis of BEDDAB is shown in Scheme 1.

Characterization of BEDDAB

FT-IR spectral analysis of BEDDAB

The FT-IR spectrum of BEDDAB is shown in Fig 1: 3401 cm⁻¹ (over tone of carbonyl group), 3068 cm⁻¹ (aromatic =C-H stretching), 2987, 2965 cm⁻¹ (symmetrical, asymmetrical C-H stretching), 1720 cm⁻¹ (>C=O stretching), 1597, 1508 and 1445 cm⁻¹ (C=C stretching vibrations of the ring), 1459 cm⁻¹ (-CH₂-N stretching), 1377 cm⁻¹ (-CH₃-N stretching), 932 cm⁻¹ (due to rocking of-CH₂ group), 922 and 747 cm⁻¹ (C-H out of plane bending vibrations of the aromatic nuclei).

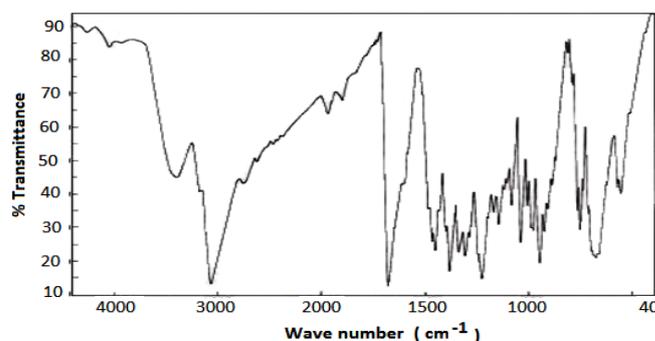


Figure 1. FT-IR Spectrum of BEDDAB

¹H-NMR spectral analysis of BEDDAB

¹H-NMR spectrum of BEDDAB is shown in Fig.2.

The following resonance signals were observed for BEDDAB: 7.57, 7.43 and 7.34 ppm (aromatic protons), 2.91 and 2.76 ppm (methylene groups attached to the carbonyl carbon and the nitrogen atom respectively), 2.53 ppm (methylene group of the decyl group which is attached to the nitrogen atom), 2.33 and 2.25 ppm (proton signals due to the methyl groups attached to the nitrogen atom), 0.95 ppm (methyl protons of the decyl group), 1.64 and 1.21 ppm (other methylene protons of the decyl group).

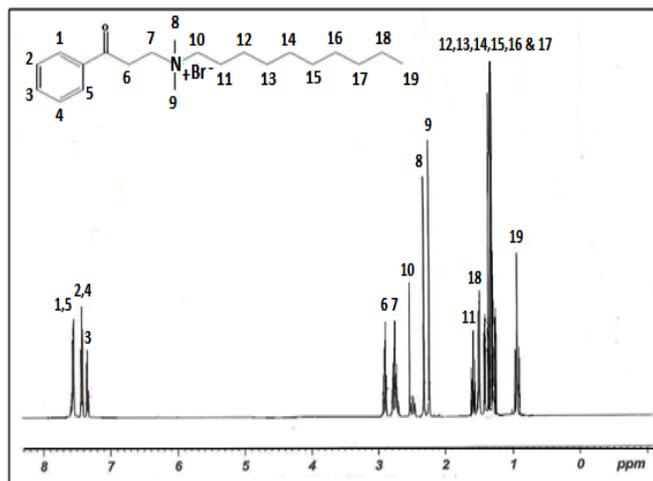


Figure 2. ¹H-NMR Spectrum of BEDDAB

¹³C-NMR spectral analysis of BEDDAB

¹³C-NMR spectrum of BEDDAB was shown in Fig.3. The following resonance signals were observed in the spectra: 200.62 ppm (carbonyl carbon), 136.24, 133.96, 128.96 and 128.88 ppm (aromatic carbons), 59.74 and 57.02 ppm (methylene carbons attached to the nitrogen atom), 43.04 ppm (methylene carbon attached to the carbonyl carbon), 46.91 ppm (methyl carbons attached to the nitrogen atom), 14.11 ppm (methyl carbon of the decyl group), 33.49, 30.94, 30.14, 28.31, 27.23 and 23.12 ppm (other methylene carbons of the decyl group)

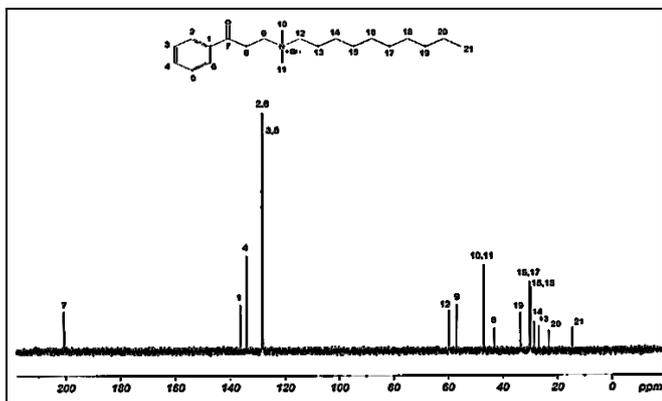


Figure 3. ¹³C-NMR Spectrum of BEDDAB

Elemental analysis of BEDDAB

Carbon, Hydrogen and Nitrogen contents of BEDDAB has

been analyzed and the results are very close to the theoretical values.

Molecular Formula: C₂₁H₃₆BrNO; Mol.Wt.: 398; Elemental analysis (%): C: 63.27 (Found): 63.31 (Calculated), H: 9.13 (Found): 9.11 (Calculated), N: 3.49 (Found): 3.52 (Calculated).

The Kinetics of Free Radical Polymerization

The kinetics of free radical polymerization of methyl and ethyl methacrylate using BEDDAB as catalyst and PDS as initiator under ethyl acetate / water biphasic media was studied under following experimental conditions.

Steady state rate of polymerization

The rate of polymerization of the monomers was ascertained by keeping the concentration of monomers 2.0 mole dm⁻³ and PDS as 2.0 x 10⁻² mole dm⁻³, volume of aqueous and organic phase as 10 ml, the concentration of sulphuric acid as 0.2 mole dm⁻³, concentration of sodium bisulphate as 0.5 mole dm⁻³ and the polymerization was started by adding 1.0 x 10⁻¹ mole dm⁻³ of BEDDAB to the aqueous phase. Table 1 shows the rate of polymerization of MMA and EMA at different time intervals.

Table 1. Steady state rate of polymerization [BEDDAB] = 1.0 x 10⁻¹ mol dm⁻³; [Monomer] = 2.0 mol dm⁻³; [H₂SO₄] = 0.2 mol dm⁻³; [NaHSO₃] = 0.5 mol dm⁻³; [PDS] = 2.0 x 10⁻² mol dm⁻³

Time, minutes	R _p × 10 ⁻⁵ , mol dm ⁻³ S ⁻¹ (MMA)	R _p × 10 ⁻⁵ , mol dm ⁻³ S ⁻¹ (EMA)
10	5.2092	3.5686
20	3.1870	2.5295
30	2.1668	1.6985
40	1.7042	1.2593
50	1.5614	1.1344
60	1.5009	1.1301

Fig. 4 shows the plot of rate of polymerization versus time intervals. The steady state rate of polymerization was arrived from the plot and it has been fixed as 50 minutes for both methyl methacrylate and ethyl methacrylate using BEDDAB as PTC.

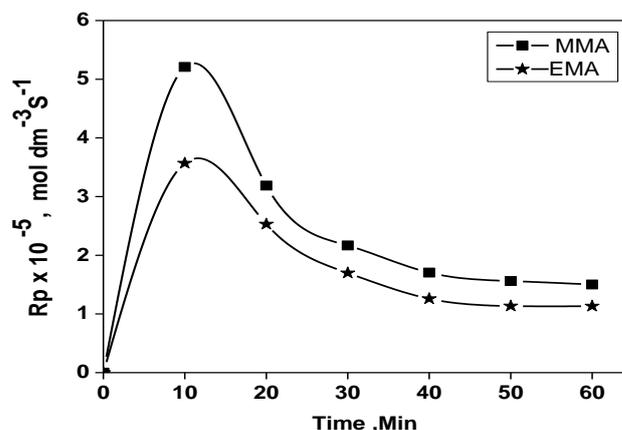


Figure 4. Plot of rate of polymerization vs. Time

Effect of monomer concentration on Rp

The effect of monomer concentration on the rate of polymerization was studied by varying the concentration in the range of 0.8 to 1.8 mole dm⁻³ by keeping the concentration of PDS as 0.02 mole dm⁻³, PTC as 0.1mole dm⁻³, ionic strength as 0.5mole dm⁻³ and pH as constant. Table 2 shows the variation of in Rp with increase in concentrations of the monomers. It was found that the Rp increases with increase in the concentration of monomers.

Table 2. Dependence of Rp on [RMA] in RMA-BEDDAB-K₂S₂O₈ [PDS] = 2.0 x 10⁻² mol dm⁻³; [BEDDAB] = 1.0 x 10⁻¹ mol dm⁻³; [H₂SO₄] = 0.2 mol dm⁻³; [NaHSO₃] = 0.5 mol dm⁻³

[RMA]mol dm ⁻³	RMA ^{0.5} mol dm ⁻³	Rp×10 ⁻⁵ mol dm ⁻³ S ⁻¹ MMA	Rp×10 ⁻⁵ mol dm ⁻³ S ⁻¹ EMA	3+ log [RMA]	6+ log Rp (MMA)	6+ log Rp (EMA)
0.8	0.8944	1.1712	0.6511	2.9031	1.0686	0.8136
1.0	1.0000	1.3578	0.7139	3.0000	1.1328	0.8536
1.2	1.1055	1.4692	0.8034	3.0790	1.1671	0.9049
1.4	1.2033	1.5465	0.8563	3.1460	1.1893	0.9326
1.6	1.2950	1.6417	0.8636	3.2040	1.2153	0.9363
1.8	1.3817	1.6826	0.9547	3.2550	1.2260	0.9798

The order of the reactions with respect to variations in concentration of monomers was determined from the slope by plotting log Rp versus log [monomer] as shown in Fig 5. The reaction orders with respect to monomer concentration for MMA and EMA were nearly half order. Also Fig 6 shows the plot of Rp versus concentration of monomer raised to suitable power passes through the origin in each case, which confirms the above observation with respect to [RMA].

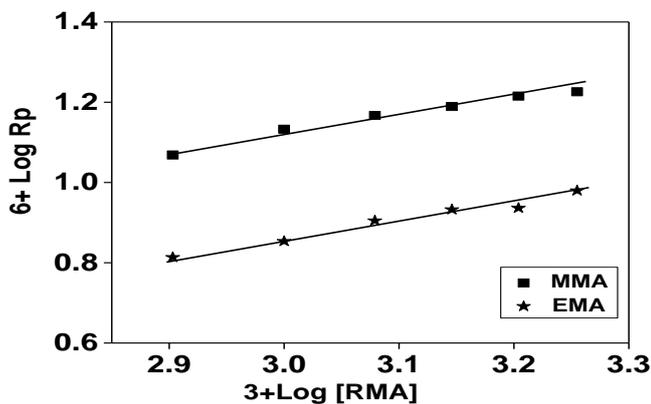


Figure 5. Plot of log Rp vs. log[RMA]

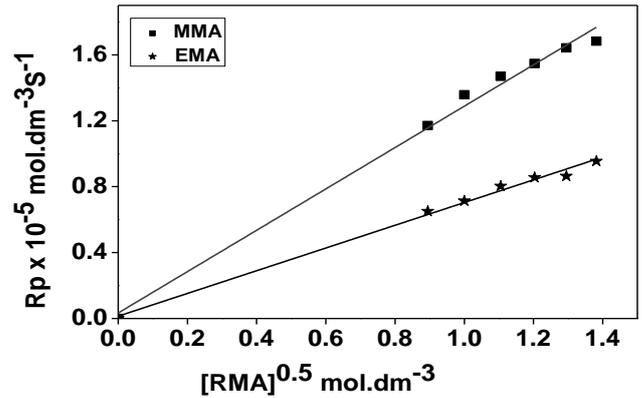


Figure 6. Plot of [RMA]^{0.5} Vs Rp

In the case of free radical polymerization of vinyl monomers, the order with respect to monomer is found to be 1.0. The deviation from the first order [19-21] with respect to monomer may be attributed to any one of the factors such as concentration of monomer involved in the initiation step, primary radical termination and occlusion phenomenon or gel effect.

Effect of initiator concentration on Rp

The effect of concentration of K₂S₂O₈ on the rate of polymerization of RMA were studied by varying the concentration of K₂S₂O₈ in the range of 0.015 to 0.025 mole dm⁻³ by keeping the concentrations of monomer as 2.0 mole dm⁻³, catalyst as 0.1mole dm⁻³ and at constant ionic strength, pH and volume ratio of aqueous to organic phase. As the concentration of PDS was increased (Table 3), Rp was found to increase. Fig 7 shows the plot of log Rp versus log [K₂S₂O₈], the order of reaction was found to be nearly unity for MMA [22, 23] and 0.7 for EMA. Fig 8 and Fig 9 show that, the plot of Rp versus [K₂S₂O₈] for MMA and EMA is linear and the line passed through the origin which confirms above observation. In the case of free radical polymerization of vinyl monomers, the order with respect to initiator is found to be square root of initiator concentration when the polymer radical terminates by mutual bimolecular reaction.

Table 3. Dependence of Rp on [K₂S₂O₈] in RMA-BEDDAB-K₂S₂O₈ [Monomer]= 2.0 mol dm⁻³; [BEDDAB] = 1.0 x 10⁻¹ mol dm⁻³; [H₂SO₄] = 0.2 mol dm⁻³; [NaHSO₃] = 0.5 mol dm⁻³;

[S ₂ O ₈ ²⁻] mol dm ⁻³	Rp×10 ⁻⁵ mol dm ⁻³ S ⁻¹ MMA	[S ₂ O ₈ ²⁻] mol dm ⁻³	Rp×10 ⁻⁵ mol dm ⁻³ S ⁻¹ EMA	3+log[S ₂ O ₈ ²⁻]	6+ log RpMMA	6+ log Rp EMA
0.015	1.4503	0.0528	0.6511	1.1761	1.1615	0.8027
0.017	1.5523	0.0577	0.6382	1.2304	1.1909	0.8087
0.019	1.8332	0.0624	0.6860	1.2788	1.2632	0.8363
0.021	1.8707	0.0669	0.7387	1.3222	1.2721	0.8684
0.023	1.9373	0.0713	0.8352	1.3617	1.2872	0.9217
0.025	2.3784	0.0756	0.8921	1.3979	1.3763	0.9504

The higher order of polymerization in the case of MMA may be either due to the induced decomposition of the initiator or due to the decrease in termination rate constant [24].

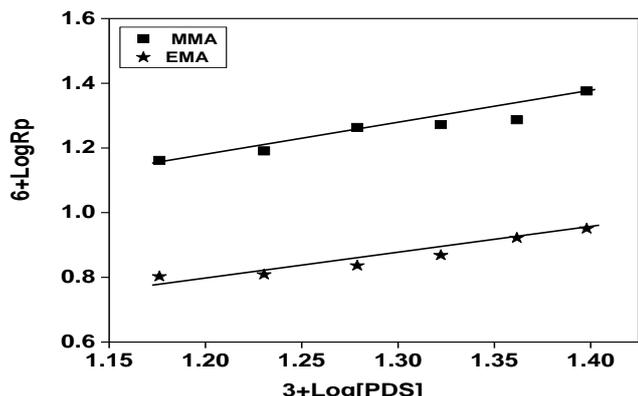


Figure 7. Plot of log Rp vs. log [PDS]

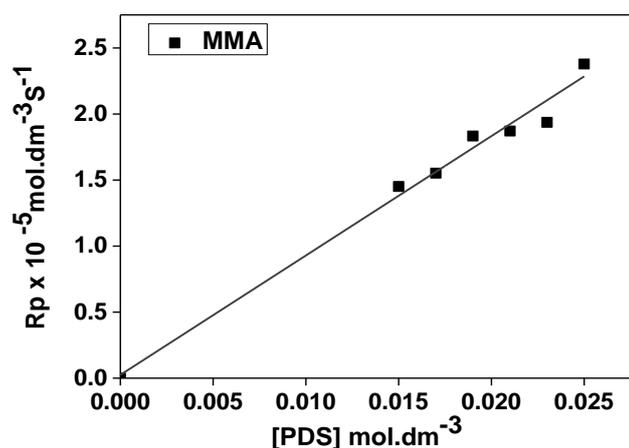


Figure 8. Plot of [PDS] Vs Rp for MMA

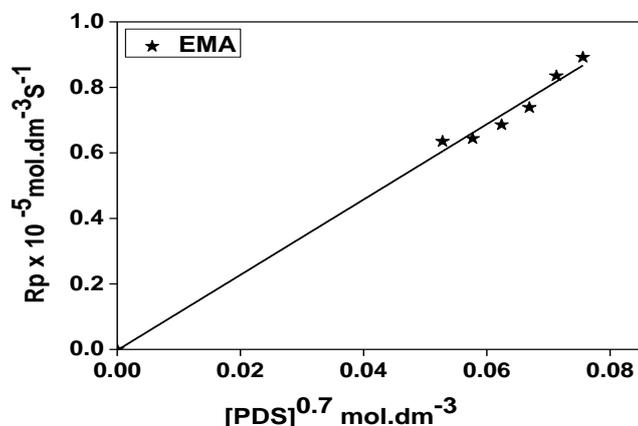


Figure 9. Plot of [PDS] Vs Rp for EMA

The induced decomposition of peroxydisulphate in the presence of oxidizable organic compounds is well known. The decomposition of PDS in water was greatly enhanced [25, 26] in the presence of methanol, ethanol, ethyl acetate etc. The

$\text{SO}_4^{\cdot-}$ ion generated in the primary decomposition even attacks the organic compounds abstracting a proton from it forming HSO_4^- and carbon centered free radicals such as $\cdot\text{CH}_2\text{OH}$ in the case of methanol and $\text{CH}_3\text{COO}\cdot\text{CHCH}_3$ and $\text{CH}_3\text{COOCH}_2\cdot\text{CH}_2$ in case of ethyl acetate.

Effect of concentration of BEDDAB on Rp

At fixed concentration of other parameters, the effect of [BEDDAB] on Rp was determined by varying its concentration in the range of 0.015-0.025 mole dm^{-3} . Table 4 shows that Rp increased with increase in concentration initially but there observed a slight decrease in Rp at higher concentration.

Table 4. Dependence of Rp on [PTC] in RMA-BEDDAB- $\text{K}_2\text{S}_2\text{O}_8$ [Monomer]= 2.0 mol dm^{-3} ; [PDS] = 2.0 x 10⁻² mol dm^{-3} ; [H₂SO₄] = 0.2 mol dm^{-3} ; [NaHSO₃] = 0.5 mol dm^{-3} ;

[PTC] mol dm^{-3}	[PTC] ^{0.5} mol dm^{-3}	Rp x 10 ⁻⁵ mol $\text{dm}^{-3}\text{s}^{-1}$ MMA	Rp x 10 ⁻⁵ mol $\text{dm}^{-3}\text{s}^{-1}$ EMA	3+ log [BEDDAB]	6+ log RpMMA	6+ log Rp EMA
0.015	0.1225	1.6699	0.6300	1.1761	1.2227	0.7993
0.017	0.1304	1.7344	0.6556	1.2304	1.2391	0.8166
0.019	0.1378	1.8231	0.6860	1.2788	1.2608	0.8363
0.021	0.1449	2.0101	0.7521	1.3222	1.3032	0.8763
0.023	0.1517	1.8272	0.7351	1.3617	1.2618	0.8663
0.025	0.1581	1.8187	0.7345	1.3979	1.2598	0.8609

A leveling off tendency was shown at higher concentration. This same leveling off tendency was also reported [27, 28] when the concentration of PTC reached maximum in the radical polymerization of alkyl methacrylates using potassium peroxydisulphate as initiator.

Fig 10 shows the order with respect to the concentration of the catalyst which was found to be around 0.5 from the plot of log Rp versus log [PTC]. The plot of Rp versus [PTC]^{0.5} was found to be linear passing through the origin confirming the above results which is shown in Fig 11. In the absence of PTC it has been observed that there was no polymerization reaction even after several hours.

In the present case a slight decrease in rate of polymerization which is observed as the concentration reached maximum may be attributed to steric hindrance of bulky benzyl group in the catalyst. This bulky group would have hampered the effective transfer of anion to the organic phase at higher concentrations. At higher concentration of the catalyst there will be interaction of the positively charged carbonyl carbon and the negatively charged oxygen atom with anion and cation of another catalyst molecule and this may also offer steric resistance for the transfer of anion to the growing chain. Therefore the rate does not increase beyond a limit due to which leveling off tendency is observed.

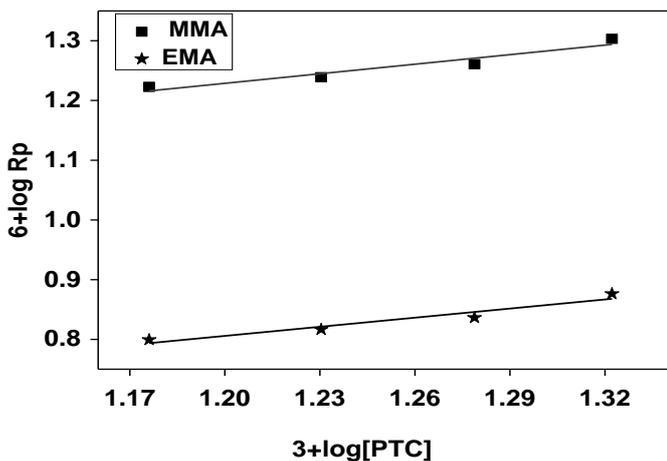


Figure 10. Effect of [PTC] on Rp

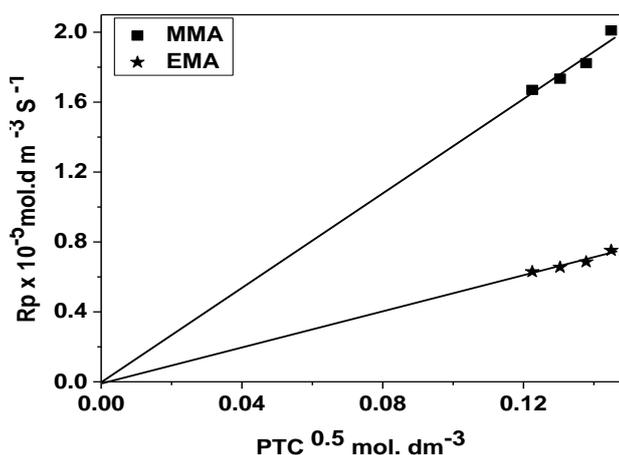


Figure 11. Plot of [PTC]^{0.5} Vs Rp

Effect of variation of temperature on Rp

The influence of temperature in the range 50 to 65°C on the rate of polymerization was studied at fixed concentration of monomer, initiator, catalyst, acid strength and ionic strength. Rp increased with increase in temperature as shown in Table 5. The activation energy for the overall rate of polymerization has been calculated from the slope of Arrhenius plot of log Rp versus 1/T as shown in Fig 12, based on the value of activation energy, the other thermodynamic parameters were computed in Table 6.

Table 5. Effect of Temperature on Rp in RMA-BEDDAB-K₂S₂O₈ [Monomer]= 2.0 mol dm⁻³;[BEDDAB] =1.0 x10⁻¹mol dm⁻³;[H₂SO₄] =0.2 mol dm⁻³;[NaHSO₃] =0.5 mol dm⁻³; [PDS] = 2.0 x 10⁻²mol dm⁻³;

T, K	Rp x 10 ⁻⁵ mol dm ⁻³ S ⁻¹ MMA	Rp x 10 ⁻⁵ mol dm ⁻³ S ⁻¹ EMA	1/T x 10 ⁻³ , K ⁻¹	6 + log Rp MMA	6 + log Rp EMA	T, K
323	1.5614	0.5124	3.095	1.1935	0.7096	323
328	1.7770	0.6284	3.048	1.2497	0.8184	328
333	1.8719	0.6774	3.003	1.2723	0.8308	333
338	1.9414	0.7067	2.958	1.2881	0.8492	338

Table 6. Thermodynamic Parameters for RMA-BEDDAB-K₂S₂O₈

RMA	Ea, kJ mol ⁻¹	ΔH, kJ mol ⁻¹	ΔS, J mol ⁻¹ K ⁻¹	ΔG, kJ mol ⁻¹
MMA	12.97	10.15	-152.86	61.05
EMA	18.21	16.28	-143.03	63.91

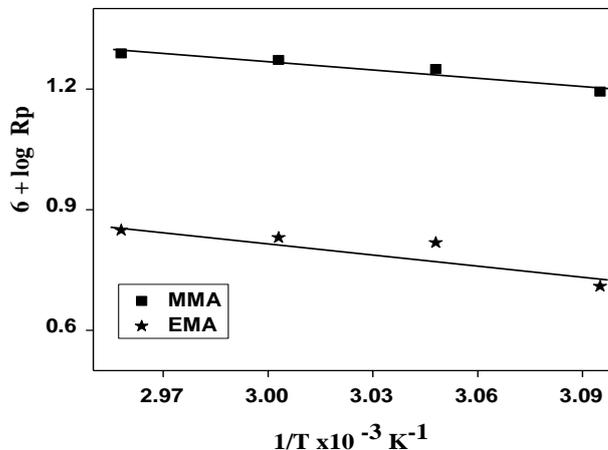


Figure 12. Arrhenius plot of MMA and EMA

The value of activation energy for the polymerization of methyl methacrylate is lower than that of ethyl methacrylate which is evident from the higher rate of polymerization of methyl methacrylate than that of ethyl methacrylate.

Product Analysis

The FT-IR spectra of the products obtained by phase transfer polymerization of MMA and EMA show the disappearance of the peak at 1635 cm⁻¹ which is originally present in the FT-IR spectrum of the monomers which suggests that the olefinic double bond is involved in the polymerization and the product is polymethyl methacrylate and ethyl methacrylate respectively.

The DSC curve of the product obtained from MMA shows an endotherm due the glass transition of poly (MMA) and the Tg value was found to be 106°C. The value is comparable to the literature value for crystalline poly (MMA) (105°C). The DSC curve of the product obtained from EMA shows an endotherm due the glass transition of poly (EMA) and the Tg value was found to be 65°C. The Tg value of the polymer depends on tacticity and molecular weight

Determination of Molecular Weight of Polyalkylmethacrylates

The molecular weight of polymers has been established by GPC technique. The number average molecular weight (Mn), weight average molecular weight (Mw) and the polydispersity index (Mw/Mn) values are shown in Table 7. The molecular weight of polymer which has been synthesized by using BEDDAB at low concentration of monomer and fixed concentrations of initiator and PTC are denoted as poly(alkyl methacrylate-L) and those synthesized at higher concentration of monomer and fixed concentrations of initiator and PTC are denoted as poly(alkyl methacrylate-H).

Table 7. Dependence of Mol. Wt. on [RMA] in RMA-BEDDAB-K₂S₂O₈

Polymer	M _n	M _w	M _w /M _n
PMMA-L	26865	50770	1.89
PMMA-H	41205	75405	1.83
PEMA-L	15810	29270	1.85
PEMA-H	34150	62155	1.82

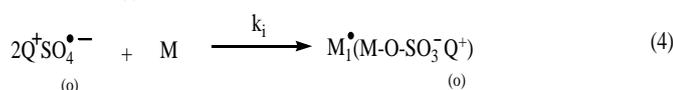
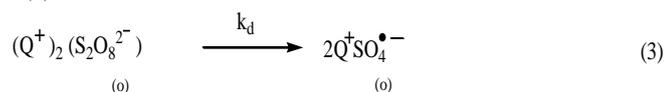
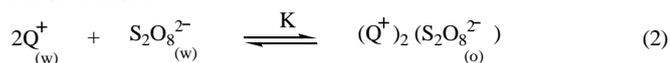
The poly index values of both poly methyl methacrylate and poly ethyl methacrylate suggest that the chain termination takes place predominantly by disproportionation [29, 30]. The Molecular weight of poly methyl methacrylate formed is found to be greater than that of poly ethyl methacrylate. As the rate of polymerization of methyl methacrylate is found to be greater than that of ethyl methacrylate this trend may be observed which is attributed to the difficulty in the chain propagation in the polymerization of ethyl methacrylate than methyl methacrylate. Molecular weight of the polymers increased as the concentration of the monomers increased.

Kinetic Scheme and Mechanism

Scheme 2 represents the kinetic investigation of the polymerization of alkylmethacrylates(M) initiated by K₂S₂O₈/PTC in ethyl acetate / water biphasic system.

The subscripts (w) and (o) represent aqueous and organic phases. k_i, k_p and k_t refer to the rate of initiation, rate of propagation and rate of termination and Q represent phase transfer catalyst.

Phase transfer



Initiation/Propagation



Termination



Based on the mechanism the rate of polymerization for RMA catalyzed using BEDDAB has been derived as

$$R_p = k_p \left[\frac{k_d K}{k_t} \right]^{1/2} \frac{[M][S_2O_8^{2-}]^{1/2}[Q^+]_{total}}{1 + K[Q^+]_w[S_2O_8^{2-}]_w} \quad (7)$$

The above equation satisfactorily explains all the experimental results and observations. The increase in R_p with increase in [PTC] and [K₂S₂O₈] may be due to an increase in the amount of Q₂S₂O₈ transferred to the organic phase, which in turn increase the number of SO₄^{•-} radical ions.

Conclusion

A new single site phase transfer catalyst, 2-benzoyl ethyl decyldimethylammonium bromide was prepared and characterized using spectroscopic techniques. The kinetics of free radical polymerization of alkyl methacrylate initiated by K₂S₂O₈ was studied using newly synthesized single site PTC in ethylacetate / water biphasic media under inert condition. Rate of polymerization was evaluated at different concentration of monomer, initiator, PTC and temperature. The order with respect to monomer was found to be 0.5 and around unity with respect to initiator, half order with respect to single site PTC. Based on the results obtained a suitable kinetic mechanism has been proposed. Molecular weight of PMMA was found to be high at higher concentration of monomer and at fixed concentrations of initiator and PTC. The formation of polymers was confirmed by FT-IR analysis.

References

- [1] C. M. Starks, C. Liotta, and M. Halpem, Phase transfer catalysis: Fundamentals, applications and industrial perspectives, Chapman and Hall, New York, Chap. 1, 1994.
- [2] E. V. Dehmlow, and S. S. Dehmlow, Phase transfer catalysis, 3rded., Verlag Chemie, Weinheim, Germany, Chap. 1, 1993.
- [3] C. M. Starks, and C. Liotta, Phase transfer catalysis: Principles and techniques, Academic Press, New York, and Chap. 1, 1978.
- [4] M. Makosza, "Two-Phase reactions in the chemistry of carbanions and halocarbenes: A useful tool in organic synthesis," Pure Appl. Chem. Soc., vol. 43, pp. 439-447, 1975.
- [5] M. J. Umopathy, and T. Balakrishnan, "Kinetics and mechanism of polymerization of methyl methacrylate initiated by phase transfer catalyst-ammonium perdisulfate system," J. Polym. Mater, vol. 15, pp. 275-278, 1998.
- [6] M. J. Umopathy, and D. Mohan, "Studies on phase transfer catalysed polymerization of acrylonitrile," Hung. J. Ind. Chem., 27, pp. 245-250, 1999
- [7] M. J. Umopathy, and D. Mohan, "Studies on phase transfer catalysed polymerization of glycidyl methacrylate," J. Polym. Mater, vol. 16, pp. 167-171, 1999
- [8] M. J. Umopathy, R. Malaisamy, and D. Mohan, "Kinetics and mechanism of phase transfer catalysed free radical polymerization of methyl acrylate," J. Macromol. Sci., Pure Appl. Chem., vol. 37, pp. 1437-1445, 2000.
- [9] M. J. Umopathy, and D. Mohan, "Phase transfer catalysed polymerization of butyl methacrylate using potassium peroxydisulphate as initiator-a kinetic study," Ind J Chem Tech., vol. 8, pp. 510-514, 2001.
- [10] T. Sivaramakrishnan, and K. S. Yoganand, "Phase Transfer Catalyst Assisted Free Radical Polymerization of Styrene-A Kinetic Study," IJACSA, vol. 3, pp. 56-59, 2015.

- [11] M. Dharmendra Kumar, P. KonguvelThehazhnan, M. J. Umapathy, and M. Rajendran, "Free radical polymerization of methyl methacrylate in the presence of phase transfer catalyst-a kinetic study," *Int. J. Polym. Mater.*, vol. 53, pp. 95-103, 2004.
- [12] S. Savitha, M. Vajjiravel, and M. J. Umapathy, "Polymerization of butyl acrylate using potassium peroxydisulphate as initiator in the presence of phase transfer catalyst-a kinetic study," *Int. J. Polym. Mater.*, vol. 55, pp. 537-548, 2006.
- [13] M. Vajjiravel, and M. J. Umapathy, "Free radical polymerization of methyl methacrylate initiated by multi-site phase transfer catalyst-a kinetic study," *Colloid Polym. Sci.*, 286, pp. 729-738, 2008.
- [14] J. Usha, P. Shyamalavathy, and M. J. Umapathy, "Free Radical Polymerization of Acrylonitrile Using Potassium PeroxyDisulphate Initiator and a Phase Transfer Catalyst," *Int. J. Polym. Mater.*, vol. 58, pp. 99-110, 2009.
- [15] P. A. Vivekanand, and T. Balakrishnan, "Kinetics of dichlorocyclopropanation of vinylcyclohexane catalyzed by a new multi-site phase transfer catalyst," *Catal. Commun.*, vol. 10, no. 5, pp. 687-692, 2009.
- [16] K. Mohammed Mustaque, S. Jayakumar, and T. K. Shabeer. "Phase transfer catalysis: Kinetics of acrylonitrile polymerization initiated by potassium peroxomonosulfate-cetylpyridinium chloride system," *J. chem. biol. phys. sci.*, vol. 2, pp. 601-607, 2012.
- [17] G. Thangaraj, A. Ramu, and R. SayeeKannan, "Kinetics and mechanisms of phase transfer catalyst aided free radical polymerization of acrylonitrile initiated by peroxydiphosphatetetraethylammonium chloride under biphasic condition," *J. chem. biol. phys. sci.*, vol. 14, no. 4, pp. 3011-3014, 2014.
- [18] A. I. Vogel, *Text book of practical organic chemistry*, 5thedn. Longmans, London, Chap. 6, 1989.
- [19] G. M. Burnett, P. Evans, and H. W. Melville, "Polymerization of esters of methacrylic acid. Part I-the polymerization of n-butyl methacrylate," *Trans. Faraday Soc.*, 49, pp. 1096-1104, 1953.
- [20] G. M. Burnett, P. Evans, and H. W. Melville, "Polymerization of esters of methacrylic acid. Part 2.—the polymerization of n-propyl methacrylate," *Trans. Faraday Soc.*, vol. 49, pp. 1105-1107, 1953.
- [21] G. M. Burnett, G. G. Cameron, and M. M Zafar, "Polymerization of methyl methacrylate in solution," *Eur. Polym. J.*, vol. 19, pp. 823-830, 1970.
- [22] T. Balakrishnan, and N. Jayachandramani, "Phase transfer catalysis-free radical polymerization of methyl methacrylate using $K_2S_2O_8$ -quaternary ammonium salt catalyst system-A kinetic study," *J. Macromol. Sci. Part A Pure Appl. Chem.*, vol. 31, no. 7, pp. 847-857, 1994.
- [23] M. Vajjiravel, and M. J. Umapathy, "Multi-site phase transfer catalyst assisted radical polymerization of glycidyl methacrylate using potassium peroxydisulphate as initiator-a kinetic study," *J. Polym. Res.*, vol. 15, 235-240, 2008.
- [24] M. Ueda, S. Shouji, T. Ogata, M. Kamachi, and C. U. Pittman, "Radical initiated homo and copolymerization of α -fluoroacrylamide living radicals in homogeneous system," *Macromolecules*, vol. 17, pp. 2800-2804, 1984.
- [25] P. D. Bartlett, and J. D. Catman, "The kinetics of the decomposition of potassium persulfate in aqueous solutions of methanol," *J. Am. Chem. Soc.*, vol. 71, pp. 1419-1425, 1949.
- [26] I. M. Kolthaff, and I. K Miller, "The chemistry of persulfate. The kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium," *J. Am. Chem. Soc.*, vol. 73, pp. 3055-3059, 1951.
- [27] A. Jayakrishnan, and D. O. Shah, "Phase transfer catalyzed free radical polymerization: Kinetics of polymerization of methyl methacrylate using ammonium peroxydisulfate/hexadecylpyridinium chloride in ethyl acetate/water," *J. Polymer Sci. Polymer Chem. Ed.*, vol. 21, pp. 3201-3208, 1983.
- [28] T. Balakrishnan, and S. Damodar Kumar, "Phase transfer catalysis: Free radical polymerization of acrylonitrile using peroxomonosulfate-tetrabutylphosphonium chloride catalyst system: A kinetic study," *J. Appl. Polym. Sci.*, vol. 76, pp. 1564-1571, 2000.
- [29] H. W. Melville, B. Noble, and W. F. Watson, "Copolymerization. II. Molecular weight distribution and mean molecular weights in copolymerization," *J. Polym. Sci.*, vol. 4, pp. 629-637, 1949.
- [30] S. Teramachi, A. Hasegawa, M. Akatsuka, A. Yamashita, and N. Takemoto, "Molecular Weight Distribution and Correlation between Chemical Composition and Molecular Weight in a High-Conversion Copolymer of Styrene-Methyl Acrylate," *Macromolecules*, vol. 11, no. 6, pp. 1206-1210, 1978.