

# Efficiency of Single Site Phase Transfer Catalyst in Free Radical Polymerization of Butyl Methacrylate – A Kinetic Study

**Meena M<sup>1\*</sup>, Umapathy M. J<sup>2</sup>.**

<sup>1</sup>Department of S&H (Chemistry), R.M.K. Engineering College, Kavaraipettai, Thiruvallur Dist. Tamil Nadu, India,

<sup>2</sup>Department of Chemistry, College of Engineering, Anna University, Chennai, Tamil Nadu, India.

## ABSTRACT

*The effectiveness of single site phase transfer catalyst- 2- benzoylethyldecyldimethylammonium bromide has been studied with the help of kinetics of free radical polymerization of butyl methacrylate. The radical polymerization was catalysed with single site phase transfer catalyst, initiated by water soluble potassium peroxydisulphate initiator in ethyl acetate / water biphasic media, under inert and unstirred condition at constant temperature, 60±1°C. The dependence of rate of polymerization on various experimental conditions, different concentrations of monomer, initiator, and phase transfer catalyst was evaluated and effect of temperature as well as solvent polarity was determined. The order of the reaction with respect to monomer, initiator and phase transfer catalyst was found to be 1, 0.5 and 0.5 respectively. It was also observed that a slight increase in rate of polymerization as the polarity of solvents increased. A suitable kinetic mechanism has been suggested as per the investigational conditions. Molecular weight of the polybutyl methacrylate which has been polymerized by single site phase transfer catalyst was evaluated using gel permeation chromatographic technique.*

**Key words:** Single site phase transfer catalyst, 2- Benzoylethyldecyldimethylammonium bromide, Kinetic mechanism, Radical polymerization.

---

\* Author for correspondence: mm.sh@rmkec.ac.in

## INTRODUCTION

Green chemistry and eco-friendly synthetic methods has drawn significant attention because of rapid industrialisation. The progress in organic synthesis towards green technology enrouted many fascinating techniques. Reactions involving phase transfer catalyst has become a versatile technique because of its mild reaction conditions, large conversion, fewer by-products formation and product selectivity<sup>1-3</sup>. Though the reaction between hydrophilic and lipophilic reactants can be facilitated by appropriate aprotic solvent, phase transferred catalysed reactions allowed the usage of water, reduced or eliminated the usage of non-eco-friendly organic solvents as well as the cost has established the PTC 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<sup>4</sup> has triggered and encouraged the application of phase transfer catalyst in organic synthesis. Hence it has become anengrossing area of research. Scholars studied the success of single site phase transfer catalyst predominantly in free radical vinyl monomers involving aqueous – organic biphasic media<sup>5-17</sup>. These studies impelled us to check the efficiency of a 2- benzoylethyldecyldimethylammonium bromide (BEDDAB)<sup>18</sup> phase transfer catalyst by polymerizing BMA and its competency has been analysed by kinetic study using water soluble potassium peroxydisulphate (PDS) initiator.

## MATERIALS AND METHODS

The monomerbutyl methacrylate (Merck, Mumbai) was 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. Double distilled water was used as solvent for the biphasic system.

## POLYMERIZATION PROCEDURE

A typical polymerization of the monomer, butyl methacrylate (BMA) 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 mol dm<sup>-3</sup>) for adjusting the ionic strength and sulphuric acid (0.2 mol dm<sup>-3</sup>) 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<sup>5-9, 12, 13</sup>. 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).

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

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

### THE KINETICS OF FREE RADICAL POLYMERIZATION

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

### Steady State Rate of Polymerization

The rate of polymerization of the monomer was ascertained by keeping the concentration of monomer as  $2.0 \text{ mole dm}^{-3}$ , PDS as  $2.0 \times 10^{-2} \text{ mole dm}^{-3}$ , volume of aqueous and organic phase as 10 ml, the concentration of sulphuric acid as  $0.2 \text{ mole dm}^{-3}$ , concentration of sodium bisulphate as  $0.5 \text{ mole dm}^{-3}$  and the polymerization was started by adding  $1.0 \times 10^{-1} \text{ mole dm}^{-3}$  of BEDDAB to the aqueous phase. Figure 1 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 40 minutes for BMA using BEDDAB as PTC.

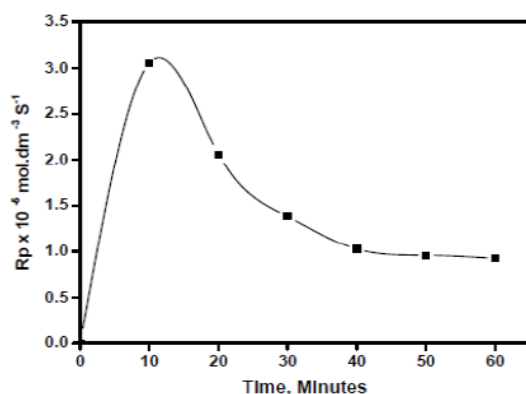


Figure 1. Rate of polymerization versus time intervals

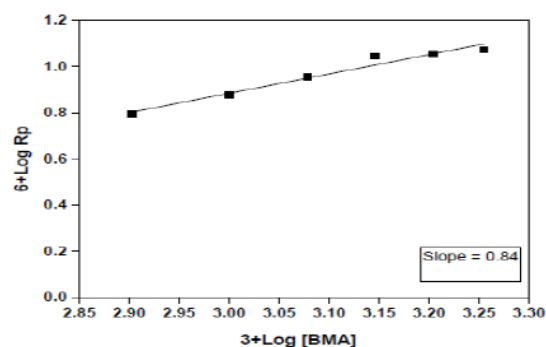


Figure 2.  $\log R_p$  versus  $\log [\text{BMA}]$

### Effect of Monomer Concentration on $R_p$

The effect of monomer concentration on the rate of polymerization was studied by varying the concentration in the range of 0.8 to  $1.8 \text{ mole dm}^{-3}$  by keeping the concentration of PDS as  $0.02 \text{ mole dm}^{-3}$ , PTC as  $0.1 \text{ mole dm}^{-3}$ , ionic strength as  $0.5 \text{ mole dm}^{-3}$  and pH as constant. It was found that, the  $R_p$  increases with increase in the concentration BMA. The order of the reaction with respect to variation in concentration of BMA was determined from the slope by plotting  $\log R_p$  versus  $\log [\text{BMA}]$  as shown in Figure 2. The reaction order with respect to monomer concentration was found to be unity. Also Figure 3 shows the plot of  $R_p$  versus concentration of monomer raised to suitable power passes through the origin, which confirms the above observation with respect to  $[\text{BMA}]$ .

In the case of free radical polymerization of vinyl monomers, the order with respect to monomer is found to be 1.0<sup>7,9,19</sup>.

### Effect of Initiator Concentration on $R_p$

The effect of concentration of  $\text{K}_2\text{S}_2\text{O}_8$  on the rate of polymerization of BMA was studied by varying the concentration of  $\text{K}_2\text{S}_2\text{O}_8$  in the range of 0.015 to  $0.025 \text{ mole dm}^{-3}$  by keeping the concentrations of monomer as  $2.0 \text{ mole dm}^{-3}$ , catalyst as  $0.1 \text{ mole dm}^{-3}$  and at constant ionic strength, pH and volume ratio of aqueous to organic phase. As the concentration of PDS was increased,  $R_p$  was found to increase. Figure 4 shows the plot of  $\log R_p$  versus  $\log [\text{K}_2\text{S}_2\text{O}_8]$ , the order of reaction was found to be 0.5. The plot of  $R_p$  versus  $[\text{K}_2\text{S}_2\text{O}_8]$  for BMA is linear (Fig. 5) 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<sup>20</sup>.

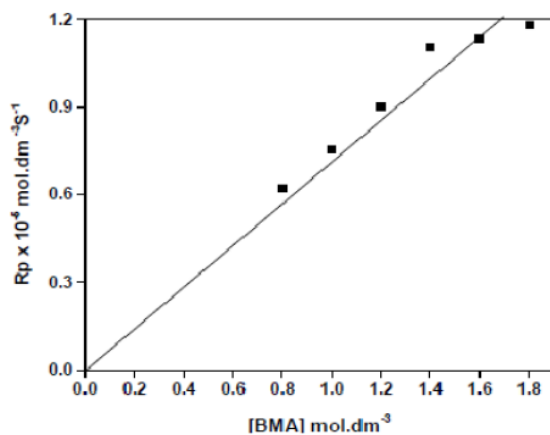
### Effect of Concentration of BEDDAB on $R_p$

At fixed concentration of other parameters, the effect of [BEDDAB] on  $R_p$  was determined by varying its concentration in the range of 0.015 – 0.025 mole  $\text{dm}^{-3}$ . Table 1 shows that  $R_p$  increased with increase in concentration initially but there observed a slight decrease in  $R_p$  at higher concentration. A levelling off tendency was shown at higher concentration. The same levelling off tendency is also reported<sup>19, 21</sup> when the concentration of PTC reached maximum in the radical polymerization of alkyl methacrylates using potassium peroxomonosulphate as initiator.

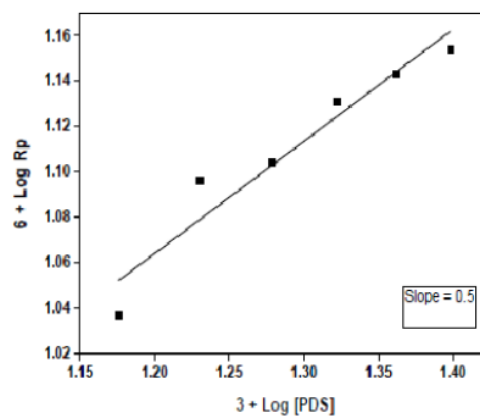
**TABLE 1. Dependence of  $R_p$  on [BEDDAB] in n-BMA-BEDDAB- $\text{K}_2\text{S}_2\text{O}_8$  System**

[BMA]	=	2.0 mol $\text{dm}^{-3}$	[ $\text{H}^+$ ]	=	0.2 mol $\text{dm}^{-3}$
[ $\text{K}_2\text{S}_2\text{O}_8$ ]	=	$2.0 \times 10^{-2}$ mol $\text{dm}^{-3}$	$\mu$	=	0.5 mol $\text{dm}^{-3}$
Temp	=	$60 \pm 1^\circ\text{C}$			

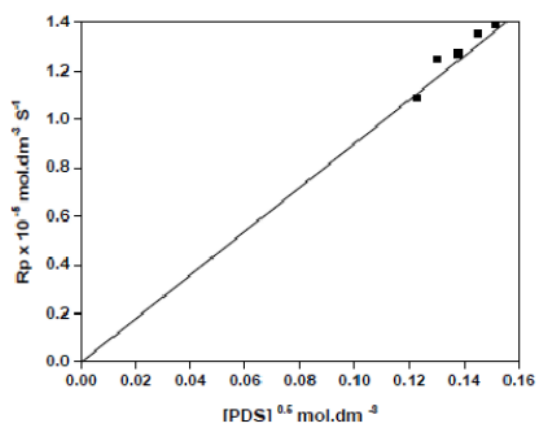
[BEDDAB] mol $\text{dm}^{-3}$	[BEDDAB] <sup>0.5</sup> mol $\text{dm}^{-3}$	$R_p \times 10^{-5}$ mol $\text{dm}^{-3} \text{S}^{-1}$	3+ log [BEDDAB]	6+ log $R_p$
0.015	0.1225	0.9796	1.1761	0.9910
0.017	0.1304	1.0157	1.2304	1.0068
0.019	0.1378	1.0283	1.2788	1.0121
0.021	0.1449	1.1712	1.3222	1.0686
0.023	0.1517	1.1421	1.3617	1.0577
0.025	0.1581	1.1385	1.3979	1.0563



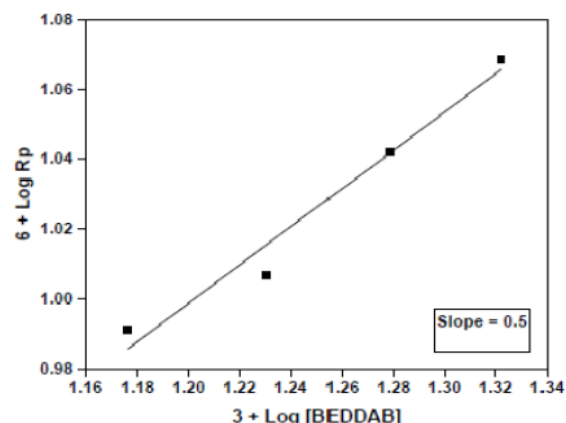
**Figure 3.**  $R_p$  versus concentration of monomer



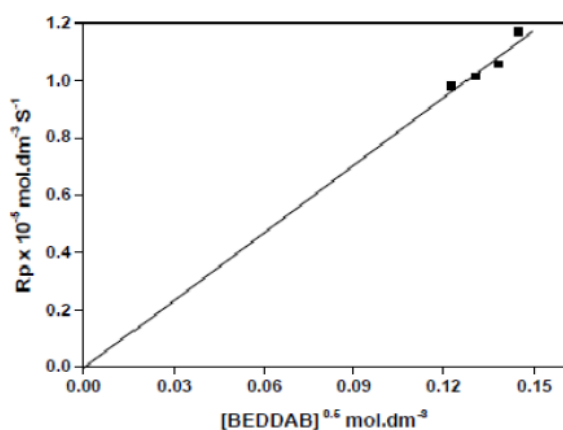
**Figure 4.** log  $R_p$  versus log [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>]



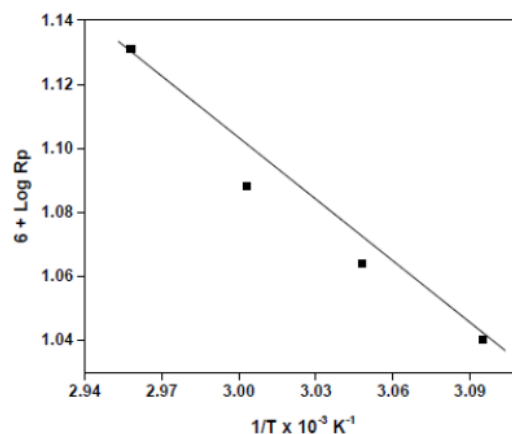
**Figure 5.**  $R_p$  versus  $[K_2S_2O_8]$  for BMA



**Figure 6.**  $\log R_p$  versus  $\log [PTC]$



**Figure 7.**  $R_p$  versus  $[PTC]^{0.5}$



**Figure 8.**  $\log R_p$  versus  $1/T$

Figure 6 shows the order with respect to the concentration of the catalyst which was found to be around 0.5 from the plot of  $\log R_p$  versus  $\log [PTC]$ . The plot of  $R_p$  versus  $[PTC]^{0.5}$  was found to be linear passing through the origin confirming the above results which is shown in Figure 7. 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 was 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 levelling off tendency was observed.

### Effect of Variation of Temperature on $R_p$

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.  $R_p$  increased with increase in temperature as shown in Table 2.

**TABLE 2. Effect of Temperature on Rp in BMA-BEDDAB-K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> System**

T, K	Rp x 10 <sup>-5</sup> mol dm <sup>-3</sup> S <sup>-1</sup>	1/T x 10 <sup>-3</sup>	6 + log Rp
323	1.097	3.095	1.0402
328	1.132	3.048	1.0538
333	1.197	3.003	1.0781
338	1.352	2.958	1.1309

The activation energy \_\_\_\_\_ for the overall rate of polymerization has been calculated from the slope of Arrhenius plot of log Rp verses 1/T as shown in Figure8, based on the value of activation energy, the other thermodynamic parameters were computed in Table 3.

**TABLE 3. Thermodynamic Parameters for n-BMA-BEDDAB-K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> System**

RMA	Ea, kJ mol <sup>-1</sup>	ΔH, kJ mol <sup>-1</sup>	ΔS, J mol <sup>-1</sup> K <sup>-1</sup>	ΔG, kJ mol <sup>-1</sup>
BMA	12.97	9.67	-157.7	62.18

### Effect of Solvent Polarity on Rp

The monomer, BMA was polymerized using three different solvents viz cyclohexane, ethyl acetate and cyclohexanone whose dielectric constants values are 2.02, 6.02 and 18.03 respectively. The rate of polymerization was found to increase in the following order, Cyclohexane < Ethyl acetate < Cyclohexanone

Figure9 shows the influence of polarity and dielectric constant of the on rate of polymerization. It is observed that, as dielectric constant of the medium increases, rate of polymerization also increases. This increase may be attributed to the greater migration of sulphate ion into the organic phase due to increase in solvent polarity<sup>11, 13 and 22</sup>.

### Product Analysis

The FT-IR spectra of the products obtained by phase transfer polymerization of BMA showed the disappearance of the peak at 1635 cm<sup>-1</sup> which was originally present in the FT-IR spectrum of the monomer which suggested that the olefinic double bond was involved in the polymerization and the product was polybutyl methacrylate.

The DSC curve of the product obtained from BMA showed an endotherm due the glass transition of poly (BMA) and the Tg value was found to be 196 °C. The Tg value of the polymer depends on tacticity and molecular weight.

### Determination of Molecular Weight of Polybutyl Methacrylate

The molecular weight of polymer has been established by GPC technique. The number average molecular weight (Mn), weight average molecular weight (Mw) and the polydispersity index (Mw/Mn) values were shown in Table 4. The molecular weight of polymer which has been synthesized using BEDDAB at low concentration of monomer and fixed concentrations of initiator and PTC is denoted as poly(butyl methacrylate - L) and the polymer synthesized at higher concentration of monomer and fixed concentrations of initiator and PTC is denoted as poly(butyl methacrylate - H).

**TABLE 4. Dependence of Mol.Wt. on [BMA] in BMA-BEDDAB -K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> System**

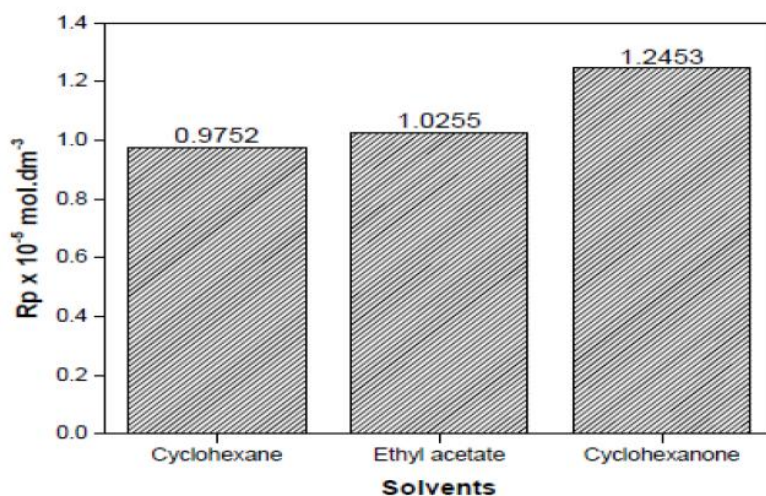
Polymer	M <sub>n</sub>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>
PBMA -L	11291	14415	1.276
PBMA -H	37221	51525	1.384

The poly index value of polybutyl methacrylate suggest that the chain termination takes place predominantly by disproportionation<sup>23, 24</sup>. It was observed that molecular weight of the polymer increased as the concentration of the monomer increased.

### Mechanism

The following observations have been made from the results of free radical polymerization of butyl methacrylate with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as initiator and single site phase transfer catalyst, 2-benzoylethyldecyldimethylammonium bromide as the phase transfer catalyst.

1. The reaction exponent with respect to [monomer] = 1
2. The order with respect to [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 0.5
3. The order with respect to [BEDDAB] = 0.5
4. An increase in R<sub>p</sub> as the dielectric constant of the solvent is increased.
5. The rate of polymerization is independent of ionic strength (μ), and [H<sup>+</sup>]



**Figure 9.** Influence of polarity and dielectric constant on rate of polymerization

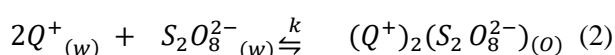
To explain the above experimental results and observations, an appropriate mechanism has been proposed.

### Kinetic Scheme

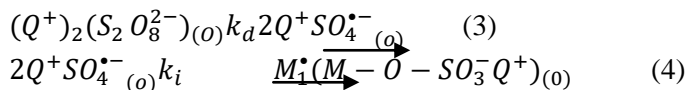
Scheme 2 represents the kinetic investigation of the polymerization of butyl methacrylate (M) initiated by K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/ PTC in ethyl acetate / water biphasic system.

The subscripts (w) and (o) represent aqueous and organic phases. k<sub>i</sub>, k<sub>p</sub> and k<sub>t</sub> refer to the rate of initiation, rate of propagation and rate of termination and Q represent phase transfer catalyst.

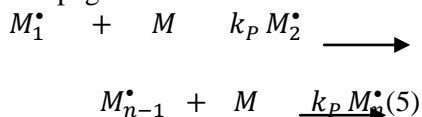
Phase transfer



Initiation



Propagation



Termination



Based on the mechanism the rate of polymerization for BMA catalysed 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 derived expression satisfactorily explains all the experimental observations.

## CONCLUSION

The kinetics of free radical polymerization of butyl methacrylate catalysed by 2-benzoyl ethyl decyldimethyl ammonium bromide as the phase transfer catalyst initiated by  $K_2S_2O_8$  was studied in ethyl acetate / water biphasic media under inert condition. Rate of polymerization was evaluated at different concentration of monomer, initiator and PTCs well as effect of temperature and solvent polarity were established. The order with respect to monomer was found to be unity and with respect to initiator and single site PTC as half order. Based on the results obtained a suitable kinetic mechanism has been proposed. Molecular weight of PBMA 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- Starks CM, Liotta C, Halpem M. Phase transfer catalysis: Fundamentals, applications and industrial perspectives. New York: Chapman and Hall; 1994.
- 2- Dehmlow EV, Dehmlow SS. Phase transfer catalysis. 3<sup>rd</sup> ed. Germany: Weinheim; 1993.
- 3- Starks CM, Liotta C. Phase transfer catalysis: Principles and techniques. New York: Academic Press; 1978.
- 4- Makosza M. Two –Phase reactions in the chemistry of carbanions and halocarbenes: A useful tool in organic synthesis. *Pure Appl Chem Soc.* 1975; 43:439-447.
- 5- Umapathy MJ, Balakrishnan T. Kinetics and mechanism of polymerization of methyl methacrylate initiated by phase transfer catalyst- ammonium perdisulfate system. *J Polym Mater.* 1998; 15:275-278.
- 6- Umapathy MJ, Mohan D. Studies on phase transfer catalysed polymerization of acrylonitrile. *Hung J Ind Chem.* 1999; 27:245-250.
- 7- Umapathy MJ, Mohan D. Studies on phase transfer catalysed polymerization of glycidyl methacrylate. *J Polym Mater.* 1999; 16:167-171.
- 8- Umapathy MJ, Malaisamy R, Mohan D. Kinetics and mechanism of phase transfer catalysed free radical polymerization of methyl acrylate. *J Macromol Sci Pure Appl Chem.* 2000; 37:1437-1445.
- 9- Umapathy MJ, Mohan D. Phase transfer catalysed polymerization of butyl methacrylate using potassium peroxydisulphate as initiator – a kinetic study. *Ind J Chem Tech.* 2001; 8: 510-514.



- 10- Sivaramakrishnan T, Yoganand KS. Phase Transfer Catalyst Assisted Free Radical Polymerization of Styrene - A Kinetic Study. *IJACSA*. 2015; 3:56-59.
- 11- Dharmendra KM, Konguvel TP, Umapathy MJ, Rajendran M. Free radical polymerization of methyl methacrylate in the presence of phase transfer catalyst – a kinetic study. *Int J Polym Mater*. 2004; 53: 95-103.
- 12- Savitha S, Vajjiravel M, Umapathy MJ. Polymerization of butyl acrylate using potassium peroxy disulphate as initiator in the presence of phase transfer catalyst – a kinetic study. *Int J Polym Mater*. 2006; 55:537-548.
- 13- Vajjiravel M, and Umapathy MJ. Free radical polymerization of methyl methacrylate initiated by multi-site phase transfer catalyst- a kinetic study. *Colloid Polym Sci*. 2008; 286: 729 -738.
- 14- Usha J, Shyamalavathy P, Umapathy MJ. Free Radical Polymerization of Acrylonitrile Using Potassium Peroxy Disulphate Initiator and a Phase Transfer Catalyst. *Int J Polym Mater*. 2009; 58: 99-110.
- 15- Vivekanand PA, Balakrishnan T. Kinetics of dichlorocyclopropanation of vinylcyclohexane catalyzed by a new multi-site phase transfer catalyst. *Catal Commun*. 2009;10(5):687-692.
- 16- Mohammed Mustaque K, Jayakumar S, Shabeer TK. Phase transfer catalysis: Kinetics of acrylonitrile polymerization initiated by potassium peroxomonosulfate – cetylpyridinium chloride system. *J chem biol phys sci*. 2012; 2:601-607.
- 17- Thangaraj G, Ramu A, Sayee Kannan R. Kinetics and mechanisms of phase transfer catalyst aided free radical polymerization of acrylonitrile initiated by peroxydiphosphate tetraethylammonium chloride under biphasic condition. *J chem biol phys sci*. 2014; 14 (4):3011 – 3014.
- 18- Meena M, Nanjundan S, Umapathy MJ. Free radical polymerization of methyl and ethyl methacrylates by green methodology. *IJAER*. 2016; 11(4):2177-2184.
- 19- Jayakrishnan A, Shah DO. Phase transfer catalyzed free radical polymerization: Kinetics of polymerization of methyl methacrylate using ammonium peroxydisulfate/hexadecyl pyridinium chloride in ethyl acetate/water. *J Polymer Sci Polymer Chem Ed*. 1983; 21:3201-3208.
- 20- Choi KY, Lee CY. Kinetics of bulk free radical polymerization of methyl methacrylate using potassium peroxydisulfate with 18-crown-6 as phase transfer catalyst. *Ind Eng Chem Res*. 1987; 26:2079-2086.
- 21- Balakrishnan T, Damodar Kumar S. Phase transfer catalysis: Free radical polymerization of acrylonitrile using peroxomonosulfate-tetrabutylphosphonium chloride catalyst system: A kinetic study. *J Appl Polym Sci*. 2000; 76:1564-1571.
- 22- Herriott AW, Picker D. Phase transfer catalysis. An evaluation of catalysis. *J Am Chem Soc*. 1975; 97(9): 2345-2349.
- 23- Melville HW, Noble B, Watson WF. Copolymerization. II. Molecular weight distribution and mean molecular weights in copolymerization. *J Polym Sci*. 1949;4:629 – 637.
- 24- Teramachi S, Hasegawa A, Akatsuka M, Yamashita A, Takemoto N. Molecular Weight Distribution and Correlation between Chemical Composition and Molecular Weight in a High-Conversion Copolymer of Styrene-Methyl Acrylate. *Macromolecules*. 1978; 11(6):1206 – 1210.

Received: February 03, 2016;  
Accepted: July 14, 2016