

Liquid-liquid Phase Transfer Catalysis: Comparison of Kinetic Studies Involving free Radicals on Polymerization of Butyl Methacrylate

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ABSTRACT: Kinetics and mechanism of the free radical polymerization of butyl methacrylate (BMA), using potassium peroxomonosulfate (PMS) / potassium peroxydisulfate (PDS) as a water-soluble initiators in the presence of 1, 4-bis (dimethylhexyl)ethylenediammonium bromide (DMHEDB) as a phase-transfer catalyst (PTC), were studied. The polymerization reactions were carried out under inert and unstirred conditions at constant temperature of 60 ± 1 °C in cyclohexanone / water biphasic medium. The rate of polymerization (R_p) increased with an increase in the concentration of BMA, DMHEDB, initiators (PMS / PDS). The order with respect to monomer, PTC and initiator was found to be 1.0. R_p was independent of the ionic strength and pH of the medium and also the degree of polymerization is calculated by varying the concentration of BMA. Based on the kinetic evidences a suitable mechanism is proposed and also a comparison between the two different initiators on rate of polymerization has been studied.

Keywords: Phase transfer catalyst · Free radical polymerization · Kinetics · Mechanism

INTRODUCTION

Phase transfer catalysis is potentially applicable to any process where two reactants are localized in orthogonal phases. They have been especially interesting because of the lower energy and downstream processing costs and also widely adopted in industrial processes, since they often result in faster, cleaner reactions and greatly simplified work-ups without the need for strictly anhydrous conditions or relatively expensive and difficult to recycle dipolar aprotic solvents and hence they directly or indirectly offers substantial benefits to the environment.

The basic concept of PTC is to bring incompatible reaction agents, into intimate contact by adding a catalyst. The role of PTC is to transfer the reactive anions continuously, in the form of lipophilic ion pairs with lipophilic cations supplied by the catalyst across the interface into the other phase so that the reaction can proceed [2-5]. Usually, the reactivity of reaction by phase-transfer catalysis is controlled by the reaction rate

in the organic phase and phase-transfer steps between the organic and aqueous phase, as well as the partition equilibrium of the catalysis between the two phases. The mass transfer problems as well as the kinetics are very important in the field of phase-transfer catalysis [6-12].

In the present study, the role of water-soluble initiators (PMS / PDS) is investigated from the radical polymerization of butyl methacrylate via liquid-liquid phase-transfer catalysis using 1, 4-bis (dimethylhexyl)ethylenediammonium bromide (DMHEDB) which has been synthesized.

EXPERIMENTAL

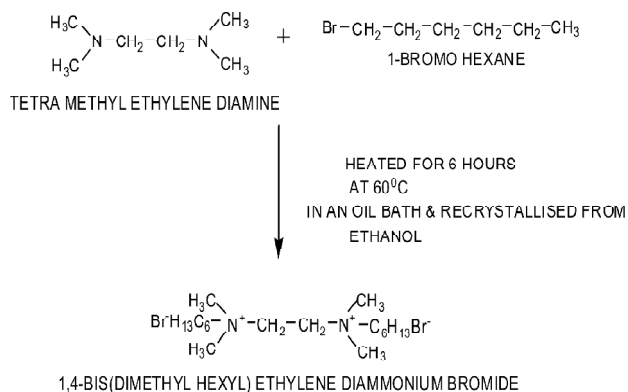
Polymerization studies were carried out in long Pyrex tubes with a provision for inlet and outlet terminals in order to isolate the reaction mixture from atmospheric oxygen. All the experiments were conducted in a thermostat bath of 20 liter capacity. The temperature of the bath was controlled by a hot wire vacuum switch relay to an accuracy of ± 0.10 °C using a toluene regulator. Water in the bath was heated electrically and stirred well by a mechanical stirrer for maintaining constant temperature throughout the

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bath. Experiments were carried out in the temperature range $60^{\circ} \pm 1^{\circ} \text{C}$. Nitrogen gas used for deaeration was freed from traces 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 monomer Butyl methacrylate (Qualigens, Mumbai), 1-bromo hexane (SRL Chemicals, Mumbai), tetra methyl ethylene diamine (SRL Chemicals, Mumbai), potassium peroxomonosulfate (Sigma Aldrich, Germany), potassium peroxydisulfate (Merck, India) were used as such. Solvents such as ethanol, cyclohexanone (Thomas Baker, Chennai) were purchased and are purified by distillation and used. Phase transfer catalyst 1, 4-bis (dimethylhexyl) ethylene diammonium bromide has been synthesized in the laboratory. Double-distilled water was used throughout the experiment for the preparation of reagents and solutions.

SYNTHESIS OF PHASE TRANSFER CATALYST (PTC)

Measured quantity of one equivalent of tetramethylethylenediamine (0.01 mol) and two equivalent of 1-bromo hexane (0.02 mol) was introduced into a 250 ml flask and were refluxed at 60°C in an oil bath along with vigorous stirring for 6 hours. The crude sample obtained was recrystallized from ethanol to get 1, 4-bis (dimethylhexyl) ethylenediammonium bromide (DMHEDB).



Scheme 1: Synthesis of Phase Transfer Catalyst

CHARACTERISATION OF DMHEDB

The Phase Transfer Catalyst, viz: 1, 4-bis (dimethylhexyl) ethylenediammonium bromide

(DMHEDAB) which was synthesized by the above procedure was characterized using IR, ^1H NMR, ^{13}C NMR and then used in the free radical polymerization.

Infrared Spectral Analysis

The IR spectrum of TMHEDB shows an absorption band at 3014 cm^{-1} showing an increase of 14 cm^{-1} from the normal value observed for C-H asymmetric stretching and also exhibits a peak at 2962 cm^{-1} for C-H symmetric stretching shows the presence of methyl and methylene group in TMHEDB. The peak at 1495 cm^{-1} is due to scissoring of methylene group. The peak at 1120 cm^{-1} is due to the presence of saturated C-N linkage. The peak at 949 cm^{-1} is due to the C-H out-of-plane bending (Fig. 1).

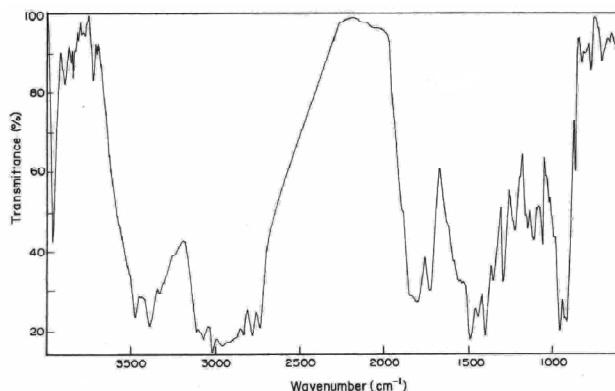


Figure 1: IR spectrum of TMHEDB

^1H NMR Spectral Analysis

The ^1H NMR spectrum exhibits the following signals. The methylene protons from tetra methyl ethylene diamine were observed as quartet at $\delta 4.6$ and the methyl proton from the same appears as singlet at $\delta 3.30$. The methylene proton next to nitrogen ($\text{N}-\text{CH}_2$) from 1-bromo hexane appears as quartet at $\delta 3.24$. The rest of the methylene proton from 1-bromo hexane produced a signal at $\delta 1.73$ to $\delta 1.33$. The terminal methyl proton appears as triplet at $\delta 1.1$ (Fig. 2).

^{13}C NMR Spectral Analysis

There are 11 signals observed in ^{13}C NMR of TMHEDB corresponding to the total number of carbon atom in the TMHEDB. The signal at $\delta 62.04$ corresponds to the very next methylene carbon atom for N which is from 1-bromo hexane. The signal at $\delta 61.57$ corresponds to methylene carbon atom from tetra methyl ethylene diamine i.e., (N-

CH₂-CH₂-N). The signal at δ 55.49, δ 55.46, δ 55.42, δ 55.26 is due to the methyl carbon from tetramethylethylenediamine i.e: 4(N-CH₃). The signal at δ 53.89, δ 53.86, δ 53.83, δ 30.50, δ 21.41 corresponds to the methylene carbon atoms from 1-bromo hexane and the signal at δ 16.27 corresponds to the terminal methyl carbon atom from the same. (Fig. 3)

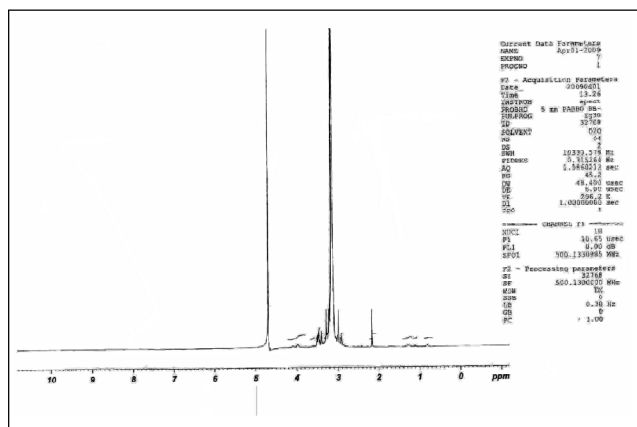


Figure 2: ¹H NMR Spectrum of TMHEDB

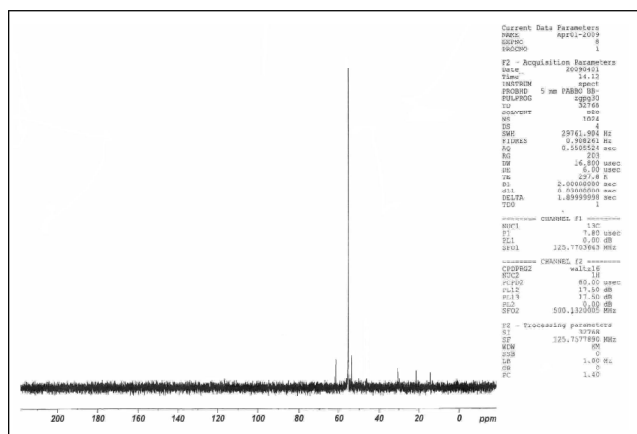


Figure 3: ¹³C NMR Spectrum of TMHEDB

POLYMERIZATION TECHNIQUE

Polymerization reactions were carried out in the reaction vessels thermostated at the desired temperature. A known amount of monomer, 1, 4-bis(dimethylhexyl) ethylenediammonium bromide (DMHEDB) were taken in the reaction tube and flushed with purified nitrogen gas for about 30 minutes to ensure an inert atmosphere. A calculated amount of deaerated initiators (PMS / PDS) solution thermostated at the experimental temperature was added to the reaction mixture and simultaneously a stop watch was started. The reaction tubes were then carefully sealed by rubber gaskets to ensure an inert atmosphere. The

reaction was arrested by pouring the reaction mixture into the vessel containing ice cold methanol. The polymer was filtered out quantitatively through a crucible (G-4), washed several times with double-distilled water and dried in a desiccator to constant weight. The rate of polymerization was computed from the weight of the polymer formed, using the following relationship:

$$R_p = 1000 * W / V * t * M$$

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

By separate experiments it was confirmed that neither (PMS / PDS) nor DMHEDB alone initiated polymerization under the experimental conditions employed.

RESULTS AND DISCUSSION

The present investigation deals with the kinetics and mechanism of phase transfer catalyst-assisted radical polymerization of Butyl methacrylate, initiated by DMHEDB-KHSO₅ initiator system and DMHEDB-K₂S₂O₈ initiator system. The polymerization reactions were carried out in cyclohexanone–water biphasic system under nitrogen atmosphere and unstirred conditions at 60°C. The dependence of the rate of polymerization (R_p) on BMA, DMHEDB, KHSO₅, K₂S₂O₈, [H⁺], ionic strength and temperature was studied.

The following salient observations were made during polymerization studies.

1. The polymerization reaction was found to be retarded by the presence of air or oxygen and hydroquinone indicating the free radical polymerization.
2. Photochemical initiation of polymerization by stray light was not observed.

STEADY STATE RATE OF POLYMERIZATION

Polymerization reactions were carried out at different time intervals at fixed concentration of BMA, 1, 4-bis (dimethylhexyl) ethylenediammonium bromide (PTC), K₂S₂O₈ / KHSO₅ and constant temperature to arrive at the steady state rate of polymerization. It has been found that at first the polymerization rate increases sharply with time, as the concentration

of radicals increases initially, but almost instantaneously, attains a constant value at which the rate of change of concentration of radicals becomes constant. The steady state rate of polymerization of butyl methacrylate using both the initiators was found to be at 50 minutes (Fig. 4, 5). To study the effects of various reaction parameters on the rate of polymerization, the polymerization was carried out for the duration of 50 minutes.

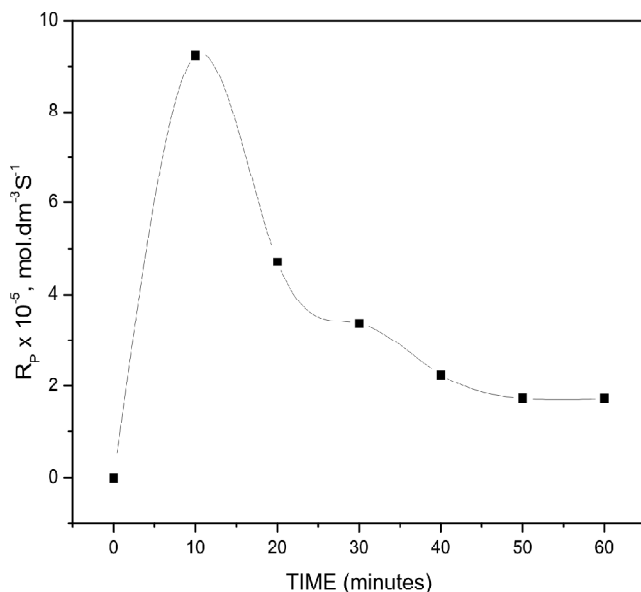


Figure 4: BMA-PTC- KHSO_5 System. Plot $R_p \times 10^{-5}, \text{mol. dm}^{-3}.\text{S}^{-1}$ vs Time, minutes Steady State Rate of Polymerization (R_p)

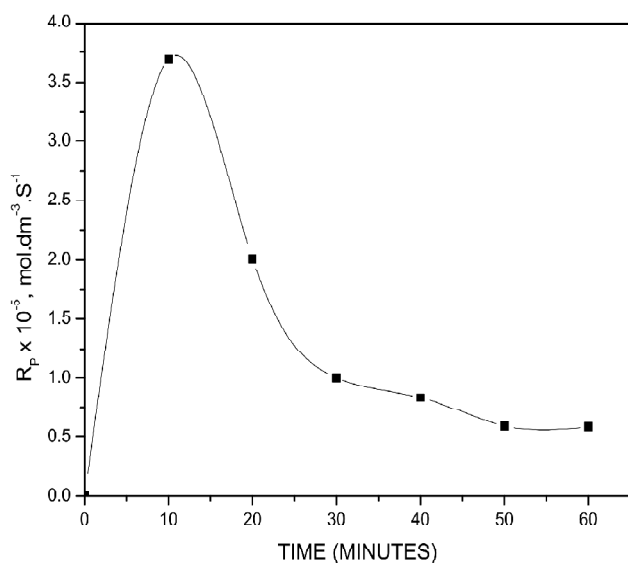


Figure 5: BMA-PTC- $\text{K}_2\text{S}_2\text{O}_8$ System. Plot $R_p \times 10^{-5}, \text{mol. dm}^{-3}.\text{S}^{-1}$ vs Time, Minutes Steady State Rate of Polymerization (R_p)

EFFECT OF MONOMER CONCENTRATION ON THE RATE OF POLYMERIZATION (R_p)

To study the effect of BMA concentration on the rate of polymerization (R_p), the concentration of BMA was varied in the range of 0.8 to 1.8 mol.dm^{-3} at fixed concentration of other components. In both KHSO_5 -PTC system and $\text{K}_2\text{S}_2\text{O}_8$ -PTC system R_p was found to increase with increase in concentration of monomer, is a consequence of gel or Trommsdorff effect and also it has been observed that the polymer particles increase in size as the monomer droplets decrease. The reaction order with respect [monomer] was determined from the slope of $\log R_p$ vs. $\log [\text{monomer}]$ (Fig. 6, 8). The reaction order with respect to monomer concentration of Butyl methacrylate was found to be 1.0 for both the systems and the reaction order was further confirmed from the straight line passing through the origin in the plot of R_p vs. [monomer] (Fig. 7 and 9).

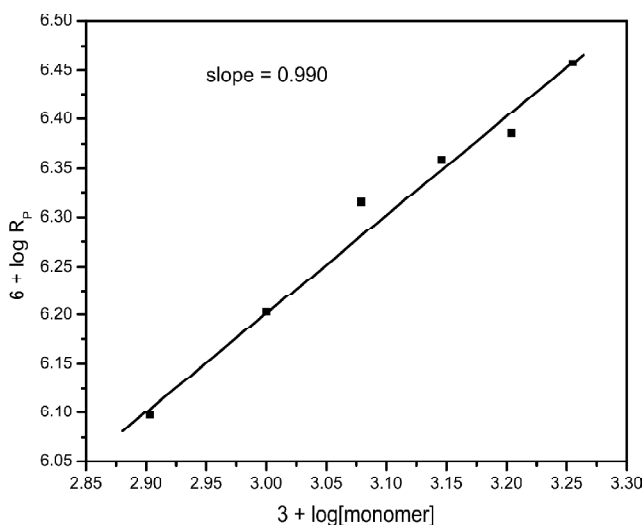


Figure 6: BMA-PTC- KHSO_5 System. Plot 2: $6 + \log R_p$ vs $3 + \log [\text{BMA}]$ Effect of Monomer Concentration on the Rate of Polymerization (R_p)

EFFECT OF INITIATOR CONCENTRATION ON THE RATE OF POLYMERIZATION (R_p)

The effect of [initiator] on R_p for both the systems was examined in the range of $1.5 \times 10^{-2} - 2.5 \times 10^{-2} \text{ mol.dm}^{-3}$ at fixed concentration of all the parameters. R_p increases with increase in the concentration of initiators in both the systems this is because as the initiator concentration increases, the rate of initiation (R_i) is sufficiently high and hence the rate of addition of monomer to the polymer chain is also tremendous. A plot of $\log R_p$

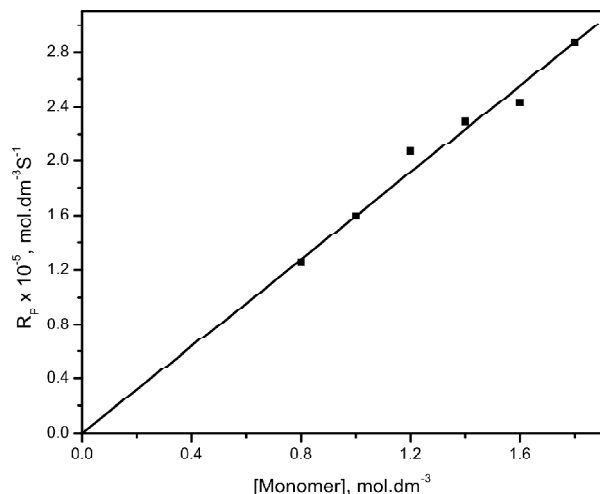


Figure 7: Conformation Plot. Plot 1: $R_p \times 10^{-5} \text{ mol.dm}^{-3}.\text{S}^{-1}$ vs [BMA] mol.dm^{-3}

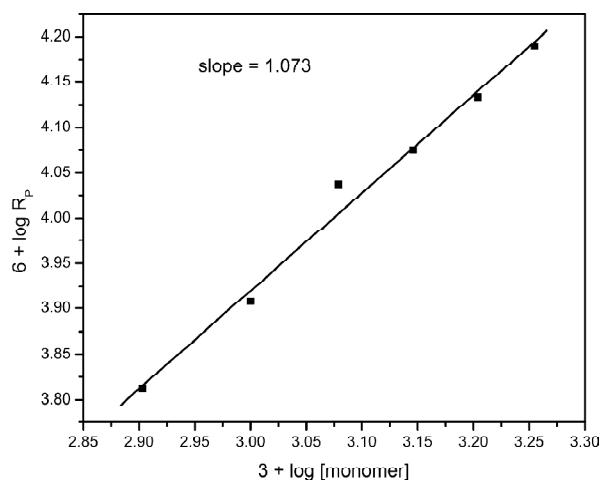


Figure 8: BMA-PTC- $\text{K}_2\text{S}_2\text{O}_8$ System. Plot 2: $6 + \log R_p$ vs $3 + \log [\text{BMA}]$ Effect of Monomer Concentration on the Rate of Polymerization (R_p)

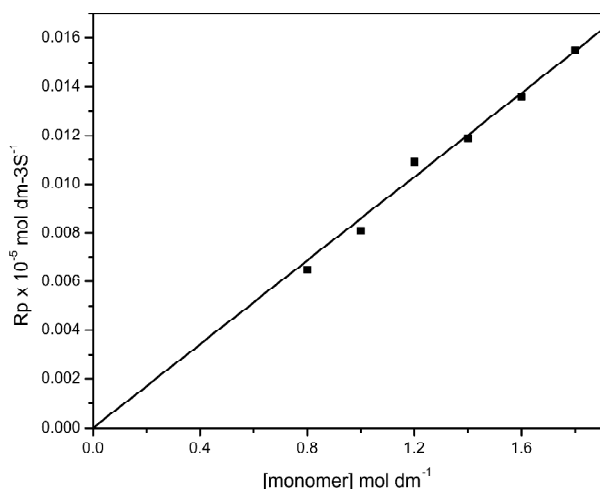


Figure 9: Conformation Plot. Plot 1: $R_p \times 10^{-5} \text{ mol.dm}^{-3}.\text{S}^{-1}$ vs [BMA] mol.dm^{-3}

vs. $\log [\text{initiator}]$ is linear with the slope of 1.0, indicating the first order dependence of R_p on initiators (Fig. 10, 12) and was further confirmed from the straight line passing through the origin in the plot of R_p vs. $[\text{initiator}]$ (Fig. 11, 13).

It has been observed that the KHSO_5 -PTC and $\text{K}_2\text{S}_2\text{O}_8$ -PTC systems were having increasing plot by employing the PTC concentration in the range of $0.75 \times 10^{-2} - 1.25 \times 10^{-2} \text{ mol.dm}^{-3}$. This is because more and more of ion pair will be formed between the initiator and DMHEDB in the aqueous phase and then it is transferred to the organic phase where it has been dissociated into radicals' hence high concentration of radical in the organic phase which in turn promotes the growth of polymer

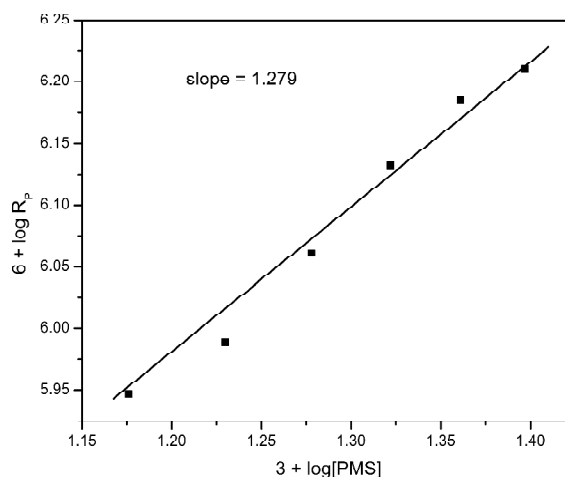


Figure 10: BMA-PTC- KHSO_5 System. Plot 2: $6 + \log R_p$ vs $3 + \log [\text{KHSO}_5]$ Effect of Initiator Concentration on the Rate of Polymerization (R_p)

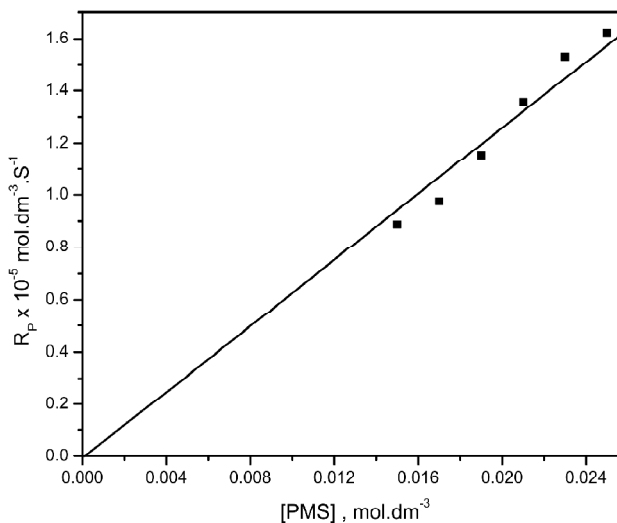


Figure 11: Conformation Plot. Plot 1: $R_p \times 10^{-5} \text{ mol.dm}^{-3}.\text{S}^{-1}$ vs $[\text{KHSO}_5] \text{ mol.dm}^{-3}$

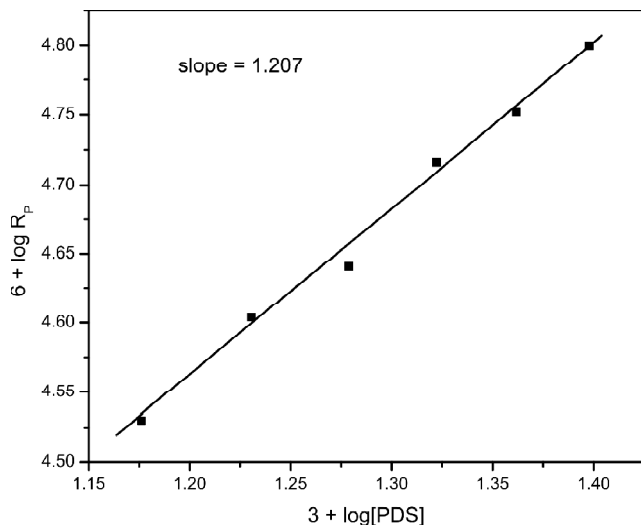


Figure 12: BMA-PTC- $K_2S_2O_8$ System. Plot 2: $6 + \log R_p$ vs $3 + \log [K_2S_2O_8]$ Effect of Initiator Concentration on the Rate of Polymerization (R_p)

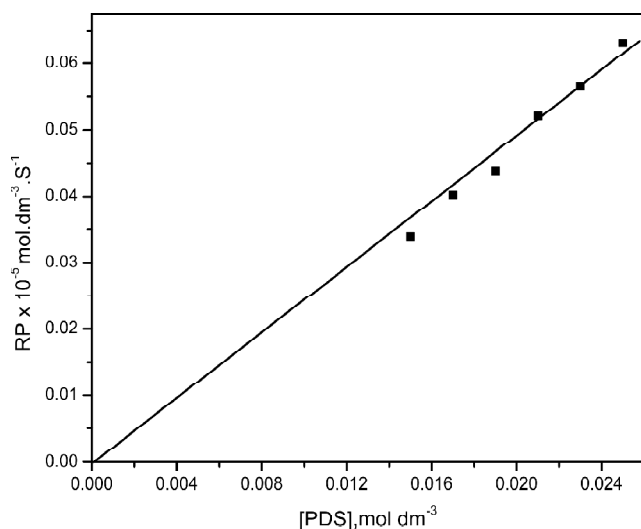


Figure 13: Conformation Plot. Plot 1: $R_p \times 10^{-5} \text{ mol.dm}^{-3}.\text{S}^{-1}$ vs $[K_2S_2O_8] \text{ mol.dm}^{-3}$ Effect of Catalyst Concentration on the Rate of Polymerization (R_p)

chain. From the slope of logarithmic plot R_p vs. PTC, the rate component with respect to PTC was found to be 1.0 (Fig.14, 16) and the straight line passing through the origin in the plot of R_p vs. PTC confirms the observed order (Fig.15, 17).

The polymerization was carried out from 323 to 338 K, in definite concentrations of BMA, initiator, PTC. The rate of polymerization increases with increase in temperature. The activation energy for the overall rate of polymerization has been computed from Arrhenius plot of $\log R_p$ vs. $1/T$. The rate of polymerization (R_p) was found to be higher in the case of $KHSO_5$ -

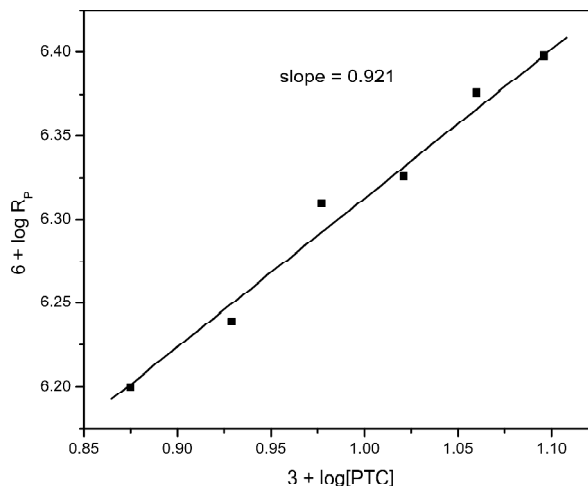


Figure 14: BMA-PTC- $KHSO_5$ System. Plot 2: $6 + \log R_p$ vs $3 + \log [PTC]$ Effect of Catalyst Concentration on the Rate of Polymerization (R_p)

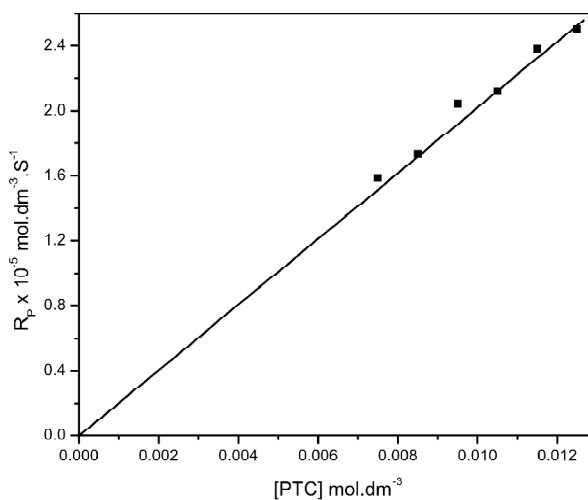


Figure 15: Conformation Plot. Plot 1: $R_p \times 10^{-5} \text{ mol.dm}^{-3}.\text{S}^{-1}$ vs $[PTC] \text{ mol.dm}^{-3}$

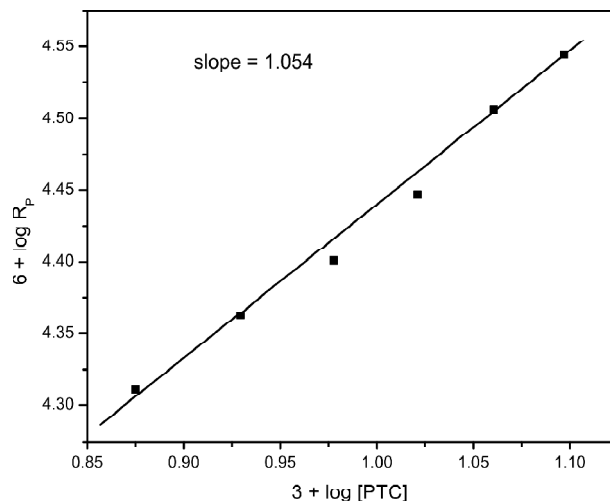


Figure 16: BMA-PTC- $K_2S_2O_8$ System. Plot 2: $6 + \log R_p$ vs $3 + \log [PTC]$ Effect of Catalyst Concentration on the Rate of Polymerization (R_p)

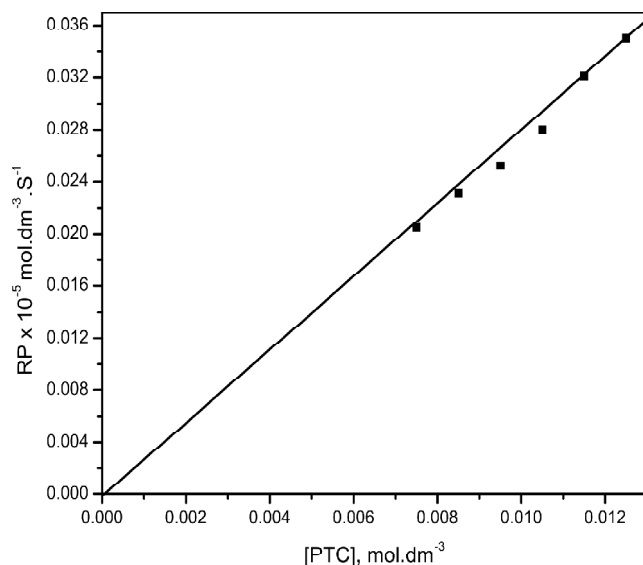


Figure 17: Conformation Plot. Plot 1: $R_p \times 10^{-5} \text{ mol.dm}^{-3}.\text{S}^{-1}$ vs $[\text{PTC}] \text{ mol.dm}^{-3}$ Effect of Temperature on Rate of Polymerization (R_p)

PTC system compared to that of $\text{K}_2\text{S}_2\text{O}_8$ -PTC system this is because in the latter case diradical is formed leading to the formation of more number of free radical and hence oligomers are formed and also the energy of activation is high whereas in the former case the $\text{OH}\cdot$ radical change the mechanism and hence decrease the apparent activation energy, thus enhancing the reaction rate.

ARRHENIUS PLOT

Polymerization reactions were carried out at four different temperatures to evaluate the energy of activation (E_a) using Arrhenius equation (Fig. 18, 19). The overall energy of activation for KHSO_5 -PTC system and $\text{K}_2\text{S}_2\text{O}_8$ -PTC system is $2.393 \text{ kJ mol}^{-1}$ and $4.966 \text{ kJ mol}^{-1}$ respectively. And also the thermodynamic parameters such as entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger), and free energy of activation (ΔG^\ddagger) have been calculated from Eyring equation (Table 1).

Table 1
Thermodynamic Parameters

	$E_a \text{ kJ/mol}$	$\Delta S^\ddagger \text{ J K}^{-1} \text{ mol}^{-1}$	$\Delta H^\ddagger \text{ kJ/mol}$	$\Delta G^\ddagger \text{ kJ/mol}$
KHSO_5 -PTC system	2.393	-183.12	0.96	61.94
$\text{K}_2\text{S}_2\text{O}_8$ -PTC system	4.966	-180.96	4.77	65.02

EFFECT OF ACID STRENGTH AND IONIC STRENGTH ON RATE OF POLYMERIZATION

Variation in acid and ionic strength of the medium had no discernable effect on the rate of polymerization for both KHSO_5 -PTC and $\text{K}_2\text{S}_2\text{O}_8$ -PTC systems.

DEGREE OF POLYMERIZATION (\bar{P}_n)

The degree of polymerization of the polymer samples were calculated using Ostwald viscometry. The concentrations of the monomers were examined under constant temperature bath to obtain the intrinsic viscosity datas. It clearly evidences that, with an increase in the monomer concentration, the degree of polymerization decreases (Figures 20, 21). A plot of $1/\bar{P}_n$ versus concentration of the monomer gives a straight line passing through the origin in BMA. Free radical initiators plays a significant role, in that the per oxo mono sulphate (PMS) generate radicals comparatively lesser than per oxo disulphate (PDS). So the number of repeating units is probably higher in the PDS.

The degree of polymerization \bar{P}_n is obtained from the derived expression for R_p as

$$\bar{P}_n = \frac{R_p}{R_t} = \frac{k_p [M][M\cdot]}{k_t [M\cdot]^2}$$

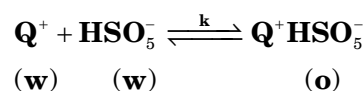
$$\bar{P}_n = \frac{k_p [M]}{2(k_t k_d K)^{1/2} [Q^+]_w [S_2O_8^{2-}]^{1/2}}$$

$$1/\bar{P}_n = \frac{2(k_t k_d K)^{1/2} [Q^+]_w [S_2O_8^{2-}]^{1/2}}{k_p [M]}$$

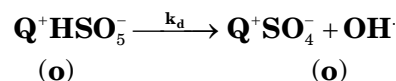
KINETIC SCHEME AND MECHANISM

(i) KHSO_5 -PTC System

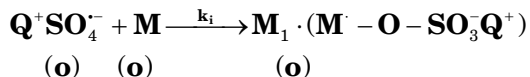
(a) Phase transfer



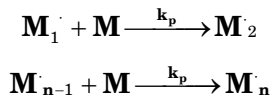
(b) Decomposition



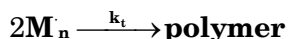
(c) Initiation



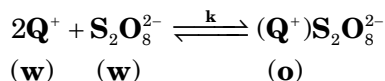
(d) Propagation



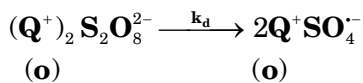
(e) Termination

(ii) $\text{K}_2\text{S}_2\text{O}_8$ -PTC System

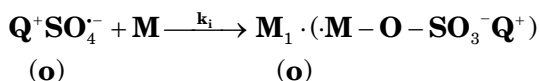
(a) Phase transfer



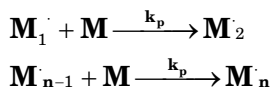
(b) Decomposition



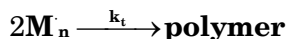
(c) Initiation



(d) Propagation



(e) Termination



This mechanism involves the formation of quaternary ammonium peroxomonosulfate complex Q^+HSO_5^- / quaternary ammonium peroxodisulfate complex $(\text{Q}^+)_2\text{S}_2\text{O}_8^{2-}$ in the aqueous phase, which is then transferred to the organic phase. The decomposition of this ion-pair takes place in the organic phase, leading to the formation of Q^+SO_4^- . Applying the general principles of free-radical polymerization and stationary-state hypothesis to the radical species, the rate law for this mechanism can be written as:

$$R_p = k_p \left(\frac{k_d K}{k_t} \right) \frac{[\text{M}][\text{HSO}_5^-][\text{Q}^+]_{\text{Total}}}{1 + k[\text{Q}^+]_w[\text{HSO}_5^-]_w}$$

$$R_p = k_p \left(\frac{k_d K}{k_t} \right) \frac{[\text{M}][\text{S}_2\text{O}_8^{2-}][\text{Q}^+]_{\text{Total}}}{1 + k[\text{Q}^+]_w[\text{S}_2\text{O}_8^{2-}]_w}$$

This expression satisfactorily explains all the experimental results and observations.

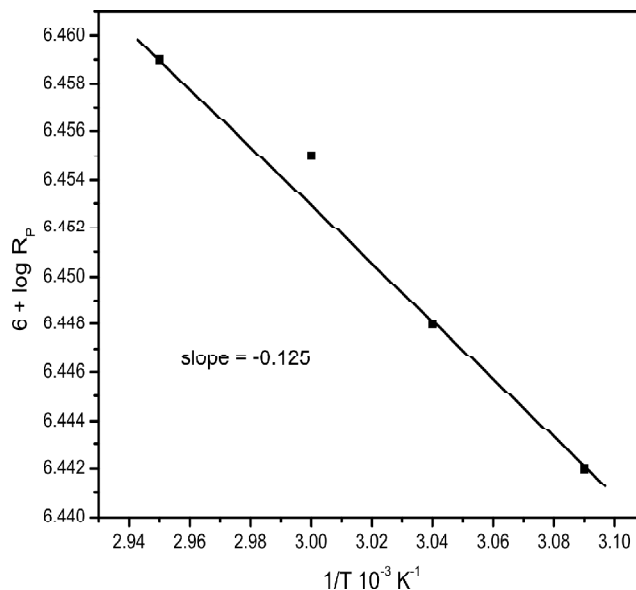


Figure 18: BMA-PTC- KHSO_5 System. Plot: $6 + \log R_p$ vs $1/T \times 10^{-3} \text{ (K}^{-1})$ Effect of Temperature on the Rate of Polymerization (R_p)

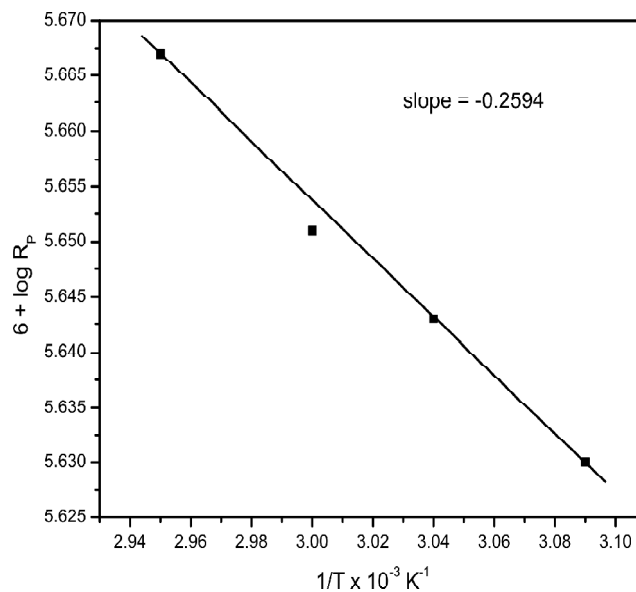


Figure 19: BMA-PTC- $\text{K}_2\text{S}_2\text{O}_8$ System. Plot: $6 + \log R_p$ vs $1/T \times 10^{-3} \text{ (K}^{-1})$ Effect of Temperature on the Rate of Polymerization (R_p)

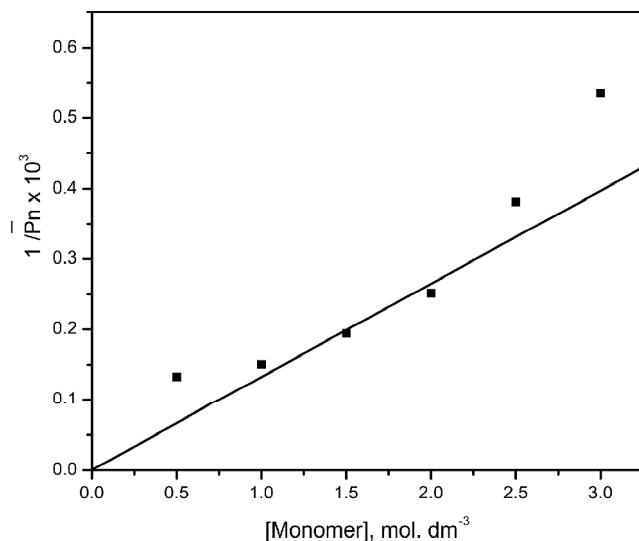


Figure 20: BMA-PTC- KHSO₅ System. Plot : $R_p \times 10^{-5} \text{ mol. dm}^{-3} \cdot \text{s}^{-1}$ vs $1/\bar{P}_n \times 10^3$ Degree of Polymerization

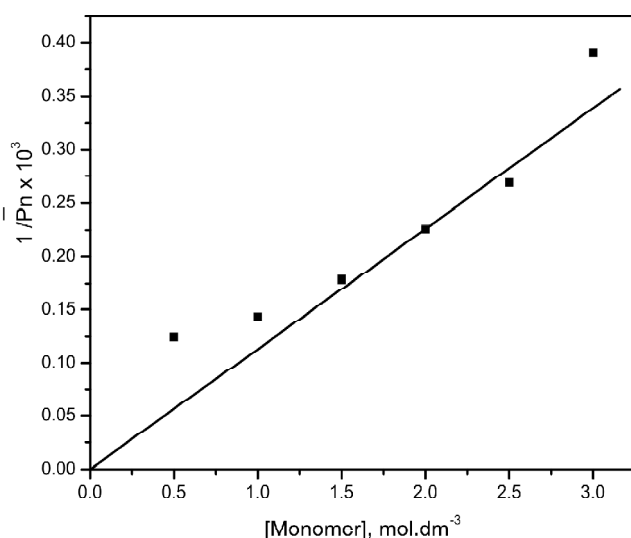


Figure 21: BMA-PTC- K₂S₂O₈ System. Plot : $R_p \times 10^{-5} \text{ mol. dm}^{-3} \cdot \text{s}^{-1}$ vs $1/\bar{P}_n \times 10^3$ Degree of Polymerization

CONCLUSION

The kinetic parameters, such as the rate of polymerization (R_p) of free radical polymerization of butyl methacrylate, increase with increasing

concentration of monomer, initiator and catalyst. The hydrogen ion concentration and ionic strength of the medium do not show any appreciable effect on the (R_p). The reaction rate increases with increasing temperature. The rate of polymerization (R_p) was found to be higher in the case of KHSO₅-PTC system compared to that of K₂S₂O₈-PTC system. The thermodynamic parameters and degree of polymerization have also been evaluated.

Reference

- [1] Sasson, Y., Neumann, R., "Handbook of Phase Transfer Catalysis", Eds.; Blackie A & P: London, **1997**.
- [2] Makosza, M., Serafinowa, B, Roczn, Chem, 39, **1965**, 1223.
- [3] Makosza, M., Wawrzyniewicz, W., Tetrahedron Lett., **1969**, 4659.
- [4] Brändström, A., Gustavii, K., Acta Chem. Scand, 23, **1969**, 1215.
- [5] Starks, C. M., *J. Am. Chem. Soc.*, 93, **1971**, 195.
- [6] Makosza, M., Fedorynski, M., Adv. Catal. 35, **1987**, 375.
- [7] Murugasen Vajjiravel, Umopathy, M .J., Coll. and Poly. Sci, 286, **2008**, 729.
- [8] Saveetha sivapitchai and Umopathy, M .J., J. App. Poly. Sci, 113, **2009**, 637.
- [9] Yoganand, K. S., Vidhya, K. R., Umopathy, M. J., *Int. J. Poly. Mat.*, 58, **2009**, 355.
- [10] Umopathy, M. J., Balakrishnan, T., *J. Polym. Mater*, 15, **1998**, 275.
- [11] Umopathy, M. J., Mohan, D., *Ind. J. Chem. Technol.*, 8, **2001**, 510.
- [12] Umopathy, M. J., Malaisamy, R., Mohan, D., *J. Macromol. Sci. Part A: Pure. App. Chem.* 37, **2000**, 1437.
- [13] Gowariker, V. R., Viswanathan, N. V., and Sreedhar, J., Polymer Science, New Age International (P) Limited, New Delhi **2003**.
- [14] Metzger, J. O., Solvent-Free Organic Syntheses, Angewandte Chemie International Edition, 37(21), **1978**, 2975.
- [15] Mieczyslaw Makosza, Phase-transfer Catalysis. A General Green Methodology in Organic Synthesis, *Pure Appl. Chem.* 72 (7), **2000**, 399.
- [16] K. S. Yoganand, D. S. Srikumar, M. Meena, and M. J. Umopathy, *Int. J. Poly. Mat.* (2009) 58, **2000**, 150.