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RESEARCH ARTICLE

PHASE TRANSFER CATALYZED POLYMERIZATION OF BUTYLMETHACRYLATE USING PEROXYDIPHOSPHATE AS AN INITIATOR – A KINETIC STUDY

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ABSTRACT

Phase transfer catalyzed free radical polymerization of butylmethacrylate (BMA), using peroxydiphosphate (PDP) as an initiator and hexadecyltrimethylammonium chloride (HDTMAC) as a phase transfer catalyst was studied. The polymerization reactions were carried out in ethyl acetate – water bi phase media at 50 ± 0.1^{0}C in an inert atmosphere under unstirred condition. The effect of various kinetic parameters such as different concentration of monomer, initiator, phase transfer catalyst (PTC) different acid strength and temperature were studied. The reaction orders with respect to monomer, initiator and the phase transfer catalyst concentrations were found to be 1, 0.5 and 0.5 respectively. The rate of polymerization (Rp) was independent of acid strength and ionic strength. Based on the experimental results obtained, a suitable mechanism has been proposed for the polymerization reaction and its significance was discussed.

INTRODUCTION

Free radical polymerization of water soluble vinyl monomers using inorganic peroxosalts have been extensively used in aqueous media. (Shamley *et al.,* 1967; Hariharan and Meenakshi 1977; Hariharan and Meenakshi 1977; Hariharan and Maruthamuthu Meenakshi 1979; Hariharan and Maruthamuthu Meenakshi1980; Hariharan and Maruthamuthu Meenakshi 1979) Recently Rasmussen and Smith (Rasmussen and Smith 1981) discovered that these salts coupled with macrocyclic crownethers could be utilized as free radical initiator for the polymerization of oil soluble monomers. They reported extensively, the polymerization of butylacrylate with different crown ethers as phase transfer catalysts and $K_2S_2O_8$ as water soluble initiator. (Rasmussen and Smith 1981) A wide variety of phase transfer catalyst - peroxo salts initiator system (Ghosh and Mandal 1985; Choiky and Lee 1987; Jayakrishnan and Shah 1983; Jayakrishnan and Shah 1984; Umapathy and Mohan 2001; Balakrishnan and Jayachandramani 1994; Balakrishnan and Jayachandramani 1996; Balakrishnan and Muniraj 1998; Balakrishnan and Arivalagan 1994; Balakrishnan and Damodarkumar 2000; Kuneida *et al.,*1982; Kuneida *et al.,* 1983; Umapathy and Balakrishnan 1998) have been demonstrated but most of the publications have dealt with peroxomono and peroxydisulphates coupled with quaternary ammonium salts as phase transfer catalysts. Phase transfer catalysis (PTC) has recommended as an efficient methodology for the synthesis of industrially important polymers with high melting point, tensile strength, and steer and stress. An interesting aspect of these reactions that a phase transfer agent coupled with peroxo salts facilitate the formation of in situ phase transfer catalyst-PMS/ PDS complex intermediate and transfer from aqueous phase to organic phase (monomer phase) where it decomposes to form active free radicals, responsible for the initiation of polymerization. Further, no similar work has yet been reported on peroxydiphosphate (PDP)–PTC initiation of polymerization. PDP is the structural and electronic analogue of peroxydisulphate and employed as redox initiator system in the presence of ascorbic acid and PDP – Ag^+ system. It has revealed some interesting features that peroxydiphosphate can function as water soluble initiator in the presence of H^+ and suitable reducing agents. In view of the fact that phase transfer catalyzed polymerizations are different from those in homogeneous reaction, not only in the mechanism and also in polymer product properties. It was considered worthful to investigate on PDP-PTC initiator system for the polymerization of vinyl monomers. The present work is concerned with a detailed kinetics and mechanism of polymerization of Butylmethacrylate (BMA) with peroxydiphosphate (PDP) as initiator and hexadecyltrimethyl ammonium chloride (HDTMAC) as PTC in biphase medium under inert atmosphere condition.

MATERIALS AND METHODS

The monomer, butyl methacrylate (BMA) was freed from the inhibitor, distilled and used for polymerization studies. The free radical initiator, potassium peroxydiphosphate ($K_2P_2O_8$) Sigma, USA. was purified by crystallization from

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deionized water. The quaternary ammonium salt, HDTMAC was used as a high purity supplied by Sigma, USA. for this study. Ethyl acetate and methanol were purified by using standard procedures. Sulphuric acid was used as a high purity analytical grade. Polymerization reactions were carried out in the presence of nitrogen atmosphere at 50±0.1^{0}C, under unstirred condition, in a long pyrex glass polymerization apparatus with a provision of gas inlet and outlet.

Polymerization procedure

The polymerization experiments were conducted in the polymerization tubes thermo stated at 50 (±) 0.1^{o}C. The aqueous phase containing phase transfer catalyst, acid (H_2SO_4) and organic phase containing monomer in the desired solvent (ethyl acetate) were taken in a polymerization tube and flushed with purified nitrogen gas to ensure inert atmosphere for 45 min. The calculated amount of deaerated PDP solution, which was also thermo stated at experimental temperature, was added to the polymerization tube quantitatively and simultaneously starting the stop watch. The polymerization tubes were then carefully sealed by rubber gaskets to ensure an inert atmosphere. The polymerizations were arrested by pouring the reaction mixture into ice cold, methanol – water mixture containing traces of hydroquinone in various experiments. (Hariharan and Maruthamuthu Meenakshi1980; Hariharan and Maruthamuthu Meenakshi 1979) Recently Rasmussen and Smith (Rasmussen and Smith 1981; Ghosh and Mandal 1985; Choiky and Lee 1987; Jayakrishnan and Shah 1983; Jayakrishnan and Shah 1984; Umapathy and Mohan 2001; Balakrishnan and Jayachandramani 1994; Balakrishnan and Jayachandramani 1996; Balakrishnan and Muniraj 1998; Balakrishnan and Arivalagan 1994; Balakrishnan and Damodarkumar 2000; Kuneida *et al.,*1982; Kuneida *et al.,* 1983). The precipitated polymer was filtered through sintered glass crucible (G.4) washed with water and methanol and dried in a vacuum oven at 60(±) 0.1^{o}C. The rate of polymerization (Rp) was calculated from the weight of the polymer obtained by using the following equation.

$$Rp = 1000 \times w / V.t.M$$

Where,

Rp - Rate of Polymerization
w - Weight of Polymer
V - Total volume of the polymerization mixture
t - Reaction time in seconds
M- Molecular weight of the monomer

In each system, temperature variations (in the range, 40 to 60^{o}C) experiments were also carried out, to evaluate the thermodynamic parameters

RESULTS AND DISCUSSION

Polymerization reactions have been carried out at 50 ± 0.1^{0}C in ethyl acetate and the induction period is found to be negligible.

Steady state rate of polymerization

The steady state rate of polymerization was first arrived by determining Rp at various time intervals and it was found to be 75 minutes (Table 1). A sharp increase in the rate of polymerization was observed initially which reached a maximum, then slightly decreased and thereafter remains constant (Fig.1). The reaction time was fixed as 75 minutes to carry out the experiments with variation in other parameters like, change in [monomer], [PTC], [initiator], variation of temperature etc.

Table 1. Steady state rate of polymerization

Reaction conditions; [BMA] : 4 mole dm^{-3}, [HDTMAC] : 5x10^{-3} mole dm^{-3}, [H$^+$] : 0.5 mole dm^{-3}, µ : 0.23 mole dm^{-3}. [PDP] : 5x10^{-3} mole dm^{-3} and Temp: 50 ± 0.1^{o}C

Time (min.)	Rp X 10^5 (mole dm^{-3} sec^{-1})
10	0.92
20	2.11
25	2.76
30	3.25
35	3.86
40	4.46
45	4.96
50	5.25
60	4.75
75	3.85
80	3.85
90	3.85
100	3.85

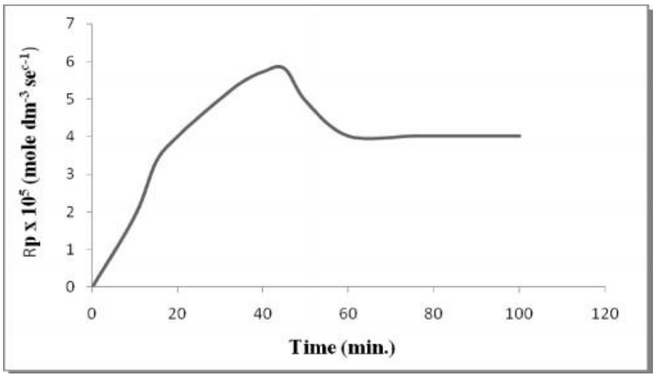


Fig.1. Steady state rate of polymerization

Effect of monomer concentration on the rate of polymerization (Rp)

The effect of monomer concentration on Rp was studied by varying [BMA] in the range of 2-5 mole dm^{-3} at fixed concentrations of initiator, catalyst, acid strength and volume ratio of aqueous to organic phase. The rate of polymerization was found to be increase with increase in monomer concentration and the order of the reaction was obtained from a plot of Rp vs. [BMA] is linear passing through the origin. The order of reaction was found to be unity in the polymerization of BMA (Table 2 and Fig.2a). A plot of 1+log [BMA] vs. 6+log Rp was found to be linear with slope 1.0 clearly indicating the dependence of Rp on [BMA] (Fig.2b). A similar orders in [monomer] were reported in the polymerization of butylmethacrylate (BMA) initiated by peroxomonosulphate, (PMS) - tetraethylammonium chloride, (TEAC), and peroxydisulphate (PDS) - PPBDAC systems respectively. (Hariharan and Meenakshi 1977; Balakrishnan and Damodarkumar 2000) Loganathan *et al*. (2012) also reported the same order of monomer concentration in the free radical polymerization of benzylmethacrylate under PTC heterogeneous condition.

Table 2. Effect of [monomer] on Rp

Reaction conditions; [PDP]: 5x10^{-3} mole dm^{-3}, [HDTMAC] : 5x10^{-3} mole dm^{-3}, [H^+] : 0.5 mole dm^{-3}, Time : 75 min., μ : 0.23 mole dm^{-3} and Temp : 50 ± 0.1°C

[BMA] (mole dm^{-3})	1+log[BMA]	RpX10^5 (mole dm^{-3} sec^{-1})	6+log Rp
2.00	1.3010	1.78	1.2504
2.50	1.3979	2.25	1.3510
3.00	1.4771	2.75	1.4400
3.50	1.5441	3.20	1.5010
4.00	1.6021	3.76	1.5316
4.50	1.6532	4.18	1.6222
5.00	1.6989	4.65	1.6701

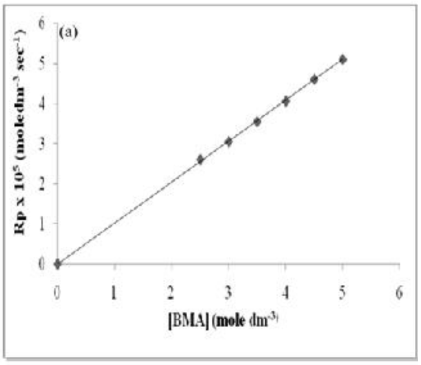


Fig.(a) [BMA] vs. Rp x 10^5

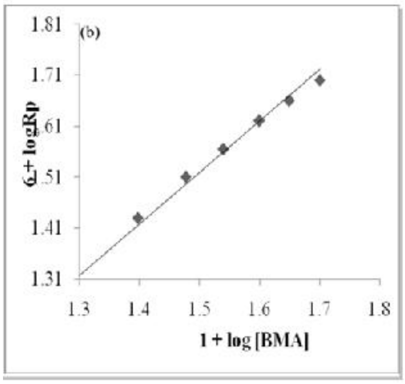


Fig.(b) 1 + log [BMA] vs. 6 + log Rp

Fig.2. Effect of [monomer] on Rp

Effect of initiator concentration on the rate of polymerization (Rp)

The effect of initiator concentration on Rp was studied by initiator concentrations in the range 0.001 – 0.008, mole dm^{-3} at fixed concentrations of monomer, catalyst, acid strength and the volume ratio of aqueous to organic phase. Rp was found to increase with increasing concentration of the initiator. The plot of Rp vs. $[PDP]^{0.5}$ is linear, indicating the half order dependence of Rp on [$K_4P_2O_8$] (Table 3 and Fig.3a). A plot of 4+log [PDP] vs. 6+logRp was half order dependence of [PDP] on Rp (Fig.3b). A similar initiator orders were observed in the polymerization of butylmethacrylate (BMA) in the presence of potassium peroxydisulphate, $K_2S_2O_8$ - PPBDAC system (Umapathy and Mohan 2001) and acrylonitrile using peroxydisulphate *et al.* (1984) also reported the same order dependence for the phase transfer catalysed free radical polymerization of methylmethacrylate (MMA) using ammonium peroxydisulphate, $(NH_4)_2S_2O_8$ – hexadecyl pyridinium chloride in ethyl acetate-water system. The same order was proposed by Kavitha *et al.* (2012) for the free radical polymerization of methylmethacrylate under multisite phase transfer catalyst.

Table 3. Effect of [initiator] on Rp

Reaction conditions ; [BMA]: 4 mole dm^{-3} , [HDTMAC] : 5x10^{-3} mole dm^{-3}, [H^+] : 0.5 mole dm^{-3}, Time : 75 min., μ : 0.23 mole dm^{-3} and Temp : 50 ± 0.1°C

[PDP] x 10^3 (mole dm^{-3})	$[PDP]^{0.5}$ x 10^3 (mole$^{0.5}$ $dm^{-1.5}$)	4 +log [PDP]	RpX10^5 (mole dm^{-3} sec^{-1})	6+log Rp
1	1.000	1.0000	0.622	0.7924
2	1.414	1.3010	0.801	0.9031
3	1.730	1.4771	0.960	0.9823
4	2.000	1.6021	1.141	1.0569
5	2.240	1.6989	1.262	1.1004
6	2.450	1.7781	1.350	1.1303
7	2.650	1.8451	1.473	1.1673
8	2.830	1.9031	1.561	1.1931

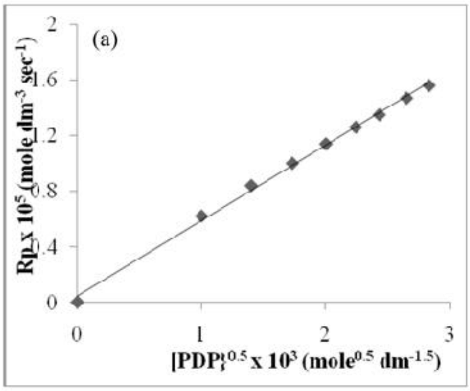


Fig.(a) $[PDP]^{0.5}$ x 10^3 vs. Rp x 10^5

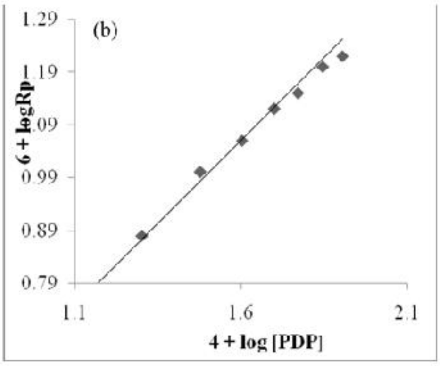


Fig.(b) 4 + log [PDP] vs. 6 + log Rp

Fig.3. Effect of [initiator] on Rp

Effect of phase transfer catalyst concentration on the rate of polymerization (Rp)

The effect of concentration of phase transfer catalyst (HDTMAC – Hexadecyltrimethyl ammonium chloride) on the polymerization rate was studied by varying the concentration of HDTMAC in the range of 0.001 – 0.008 mole dm^{-3} at definite concentrations of monomer, initiator, acid strength and the volume ratio of aqueous to organic phase. Rp is found to be increase with increase in concentration of the catalyst. The order with respect to the concentration of the catalyst is found to be around 0.5. A plot of Rp vs. [PTC]$^{0.5}$ is linear passing through the origin confirming the above result (Table 4 and Fig.4a). A plot of 4+log [HDTMAC] vs. 6+logRp was found to be linear with slope 0.5 clearly indicating the half order dependence of [HDTMAC] on Rp (Fig.4b). A similar order was observed by Balakrishnan *et al.* (2000) for the phase transfer catalyzed free radical polymerization of butylmethacrylate (BMA) using peroxomonosulphate, PMS - tetrabutylphosphonium chloride catalyst system. Umapathy and Mohan (2001) also reported the same order dependence of PTC, for the phase transfer catalyzed polymerization of butylmethacrylate (BMA) using potassiumperoxydisulphate, $K_2S_2O_8$ - PPBDAC system. The same order dependence was also reported by Balakrishnan and Jayachandramani (1996) for the free radical polymerization of methylmethacrylate (MMA) using potassium peroxydisulphate, $K_2S_2O_8$-Triethylbenzylammonium chloride, TEBAC catalyst system. The same order was also proposed by Savitha *et al.* (2009) for the synthesis of new phase transfer catalyzed free radical polymerization of ethylmethacrylate.

Table 4. Effect of [catalyst] on Rp

Reaction conditions; [BMA] : 4 mole dm^{-3}, Time :75 min., [PDP] : 5x10^{-2} mole dm^{-3}, [H$^+$] : 0.5 mole dm^{-3}, µ : 0.23 mole dm^{-3} and Temp : 50 ± 0.1^{o}C

[HDTMAC]x10^3 (mole dm^{-3})	[HDTMAC]$^{0.5}$ x 10^3 (mole$^{0.5}$ dm$^{-1.5}$)	4 +log [HDTMAC]	RpX10^5 (mole dm^{-3}sec^{-1})	6 + log Rp
1	1.000	1.0000	0.59	0.7612
2	1.414	1.3010	0.77	0.8865
3	1.730	1.4771	0.95	0.9777
4	2.000	1.6021	1.13	1.0531
5	2.240	1.6989	1.25	1.0969
6	2.450	1.7781	1.35	1.1303
7	2.650	1.8451	1.45	1.1614

Effect of variation of temperature on the rate of polymerization (Rp)

The effect of temperature on Rp was studied at different temperature in the range of 40-60°C, at fixed concentrations of monomer, initiator, catalyst acid and ionic strength. It was found that Rp increases with temperature (Table 5 and Fig.5).

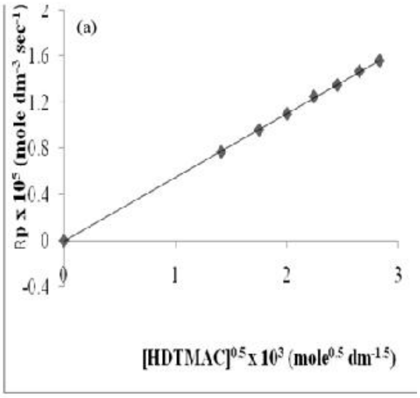


Fig. (a) [HDTMAC]$^{0.5}$ x 10^3 vs.Rp x 10^5

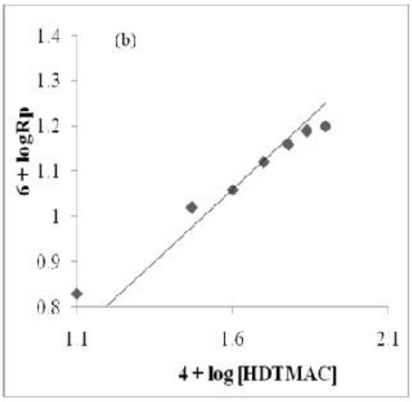


Fig.(b) 4 + log [HDTMAC] vs. 6 + log Rp

Fig.4. Effect of [catalyst] on Rp

Table 5. Effect of Temperature on Rp

Reaction conditions; [BMA] : 4 mole dm^{-3} ,Time : 75 min. ,[PDP] : 5x10^{-3} mole dm$^{-3,}$ [HDTMAC] : 5x10^{-3} mole dm$^{-3,}$ [H$^+$] : 0.5 mole dm$^{-3,}$ µ : 0.23 mole dm^{-3}

T^o C	T K	1/Tx 10^3 (K^{-1})	RpX10^5 (mole dm^{-3} sec^{-1})	8+log Rp
40	313	3.1949	2.45	3.3892
45	318	3.1446	3.16	3.4997
50	323	3.0958	3.89	3.5699
55	328	3.0488	4.79	3.6803
60	333	3.0030	5.80	3.7634

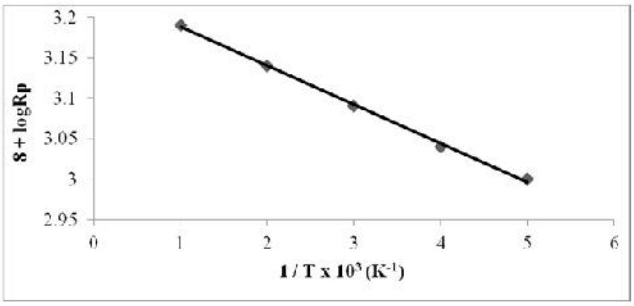


Fig.5. Effect of Temperature on Rp

Yoganand *et al.* (2011) also reported the same kinetic results for disite phase transfer catalyst assisted free radical polymerization of methylmethacrylate using water soluble $K_2S_2O_8$ as an initiator. From a plot of 8 + log Rp vs. 1 / T, energy of activation was calculated. (Ea = 9.15 kcal mole^{-1}). From the Arrhenius plot, the thermodynamic parameters were calculated to be $\Delta H^{\#}$ = 7.87 kcal mole^{-1}, $\Delta S^{\#}$ = -0.005 kcal mole^{-1} K^{-1} and $\Delta G^{\#}$ = 24.18 kcal mole^{-1}.

Effect of solvent polarity on the rate of polymerization (Rp)

The effect of solvent on Rp was examined by carrying out the polymerization reaction for BMA in three different solvents viz, ethylacetate, cyclohexane and toluene having dielectric constants of 6.02, 2.02 and 1.25 respectively. It was found that the Rp was decreased in the following order, ethyl acetate > cyclohexane > toluene (Table 6). The decrease in the rate of polymerization may be due to the increase in the polarity of the organic medium with facilitated greater transfer of peroxydiphosphate ion to the organic phase.

Table 6. Effect of Solvent polarity on Rp

Reaction conditions; [BMA] : 4 mole dm^{-3}, [HDTMAC] : 5 x 10^{-3} mole dm^{-3}, $[H^+]$: 0.5 mole dm^{-3}, μ : 0.23 mole dm^{-3}, Time : 75 min., [PDP] : 5 x 10^{-3} mole dm^{-3} and Temp : 50 ± 0.1° C

Solvent	$Rp \times 10^5$(mole dm^{-3} $sec^{-1)}$
Ethylacetate	-3.82
Cyclohexane	-3.34
Toluene	-2.34

MECHANISM AND RATE LAW

Generation of Phosphate anion free radical

The generation of phosphate anion free radical ($PO_4^{\cdot 2-}$), from $P_2O_8^{4-}$ion was found to be very similar to sulphate anion $SO_4^{\cdot -}$ from $S_2O_8^{2-}$ions. According to previous reports (Nayak and Lenka 1994; Arora and Singh 1994; Nayak *et al.*, 1980; Arai *et al.*, 1973; Morgan 1964) the formation of free radical species by the decomposition of peroxydiphosphate ion in the aqueous medium given by the following eqn (1-6).

$$P_2O_8^{4-} \overset{H^+}{\rightleftarrows} H_2P_2O_8^{2-} \overset{H^+}{\rightleftarrows} H_3P_2O_8^{-} \quad \text{.............. (eqn.1)}$$

$$H_3P_2O_8^{-} \xrightarrow{\text{slow}} H_2PO_4^{\cdot} + HPO_4^{\cdot -} \quad \text{............ (eqn.2)}$$

$$H_3P_2O_8^{-} + H_2O \xrightarrow{\text{slow}} H_2PO_4^{\cdot} + H_2PO_4^{-} + OH^{\cdot} \quad \text{........... (eqn.3)}$$

$$H_2PO_4^{\cdot} + H_2O \rightleftarrows H_3PO_4 + OH^{\cdot} \quad \text{........... (eqn.4)}$$

$$HPO_4^{\cdot -} + H_2O \rightleftarrows H_2PO_4^{-} + OH^{\cdot} \quad \text{..................... (eqn.5)}$$

$$HPO_4^{\cdot -} + OH^{\cdot} \longrightarrow H_2PO_4^{-} + \tfrac{1}{2} O_2 \quad \text{.................. (eqn.6)}$$

The hydroxyl radicals (OH) can recombine among themselves to form H_2O_2 (eqn.7).

$$OH^{\cdot} + OH^{\cdot} \longrightarrow H_2O_2 \quad \text{............... (eqn.7)}$$

The hydroxyl radicals ($OH^{\cdot}$) can recombine among themselves to form H_2O_2. Further, phosphate radicals can be produced efficiently by one electron reduction of peroxydiphosphate, eg with hydrated electron (Balakrishnan and Jayachandramani 1996) (eqn.8).

$$P_2O_8^{4-} + e^{(-)}_{aqu} \longrightarrow PO_4^{\cdot 2-} + PO_4^{3-} \quad \text{.............. (eqn.8)}$$

(or)

By direct UV photolysis of the peroxide ion[31-32] (eqn.9)

$$P_2O_8^{4-} \xrightarrow{h\gamma} 2PO_4^{\cdot 2-} \quad \text{............... (eqn.9)}$$

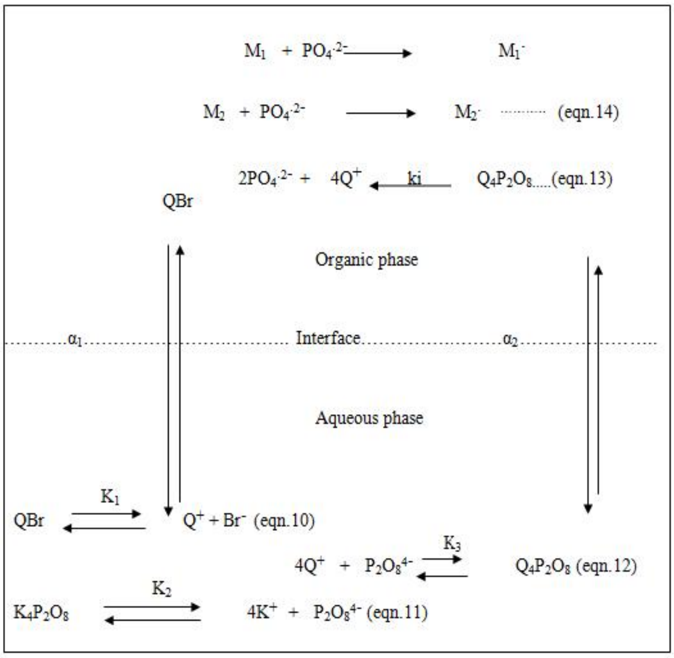
Phosphate radicals exists in three acid-base forms with pka values 5.9 or 8.9. (Balakrishnan and Muniraj 1998). These forms can react with organic compounds by abstracting hydrogen, adding to unsaturated compounds or by oxidizing by one electron transfer. The known rate constants initiate differences in the reactivity of phosphate radical species, suggesting that the oxidizing power decreases in the order,

$H_2PO_4^{\cdot}$ > $HPO_4^{\cdot -}$ > $PO_4^{\cdot 2-}$ (Jayakrishnan and Shah 1983; Balakrishnan and Arivalagan 1994)

Further, peroxydiphosphate ions bear a strong resemblance to peroxodisulphate ions, i.e., they can produce strongly oxidizing phosphate radicals by rupture of peroxide bonds or by one electron reduction. The major difference between sulphate and phosphate radical is that the oxidizing power of the sulphate radical is pH independent in the common pH range, whereas the protonation of phosphate radical changes the formal reduction potential of the phosphate radicals. $H_2PO_4^{\cdot}$ is the strongest oxidant in the series of phosphate radicals with a reduction potential of ca.2.5.V. (Jayakrishnan and Shah 1983).

A detailed survey of literature states that,

i) Polymerization of vinyl monomers using peroxo salts coupled with- organic / inorganic reducing agents, i.e. redox pairs, account degradative chain transfer mechanism for redox initiator polymerization of vinyl monomers involving peroxydiphosphate as one of the initiating components.
ii) Polymerization of vinyl monomers using peroxosalts, assisted by phase transfer agent by many researches [11-18] and investigated free radical initiation of polymerization of vinyl monomers.
iii) The polymerization mechanisms support the Stark mechanism (Starks and Liotta1978) of bi phase (LLPTC), i.e., formation and dissociation of phase transfer catalyst - initiator complex as its transfer from aqueous phase to organic phase as initiator of monomer in organic phase.



Scheme.1. Polymerization mechanism with PTC in aqueous-organic biphase system

Considering the above decomposition of peroxyphosphate ions in aqueous or acidic medium (eqn.1-9) and scheme of polymerization reactions (eqn.10-14) and on the kinetic results obtained from the study, the following mechanism of polymerization has been proposed.

Phase Transfer

$Q^{+}_{(w)} - [H_3P_2O_8]_{(w)} \overset{K}{\rightleftarrows} [QH_3P_2O_8]_{(o)}$ ------------- (eqn 15)

Complex

Decomposition of Complex

$[QH_3P_2O_8]_{(O)} + c^{\theta}_{solvent} \xrightarrow{kd} Q^+ + 3H^+ + PO_4^{\cdot 2-}$ ---------- (eqn.16)

(Where $PO_4^{\cdot 2-} = R^{\cdot}$)

Initiation

$R^{\cdot} + M \xrightarrow{ki} RM_1^{\cdot}$ --------------- (eqn.17)

Propagation

$RM_1^{\cdot} + M \xrightarrow{kp} RM_2^{\cdot}$

$RM^{\cdot}_{(n-1)} + M^{\cdot} \xrightarrow{kp} RM_n^{\cdot}$ (eqn.18)

Termination

$RM_n^{\cdot} + RM_n^{\cdot} \xrightarrow{kt}$ Polymer ------------ (eqn.19)

Applying the steady state approximation to the species $R^{\bullet}$ and $RMn^{\bullet}$ we can derive the following expression for the rate of polymerization.

$Rp = kp\ \{2kdK / kt\}^{1/2}\ [Q^+]^{1/2}_w\ [H_3P_2O_8^-]^{1/2}_{total}\ [M]\ /\ 1 + K\ [Q^+]_w$ ----------- (eqn.20)

Equation (20) explains most of the observed kinetic data. If $1 >> K\ [Q^+]_w$, we have,

$Rp = kp\ \{2kdK / kt\}^{1/2}\ [Q^+]^{1/2}_w\ [H_3P_2O_8^-]^{1/2}_{total}\ [M]$ ------------- (eqn.21)

The above eqn.21 explains the experimental observation, i.e. Rp is directly proportional to the half power of [Initiator] and [Catalyst] and unity on [Monomer].

INSTRUMENTAL ANALYSIS OF THE OBTAINED POLYMER (PBMA)

The kinetics and the growth of the polymer PBMA can be confirmed by the following instrumental analysis.

UV-Spectroscopy

A UV spectrum (Fig.6) can be taken for the obtained polymer, by taking along the wave length (nm) in the X-axis and absorbance in the Y-axis. A peak at 272 nm reveals the presence of methyl ester group attached carbon connected with butyl substituent present in the polymer. This confirms the presence of ester functional group present in the vinyl polymer (Graybeal, Jack 1988; Kalsi 2002).

FT-IR Spectroscopy

A FT-IR spectrum of the obtained polymer can be taken along wavenumber in X-axis and % of transmittance in the Y-axis (Fig.7). A peak at 1715 cm^{-1} corresponds to the C=C stretching of the polymer. (Graybeal, Jack 1988) A peak at 1735 cm^{-1} corresponds to the symmetric stretching of the ester group. (Kalsi 2002). The peak at 3440-3610 cm^{-1} confirms the –CH stretching of the polymer. The peaks at 1260 cm^{-1} and 2740 cm^{-1} corresponds to the CH_2-CH_3 and CH_2-CH_2 stretching of the polymer (Kalsi 2002).

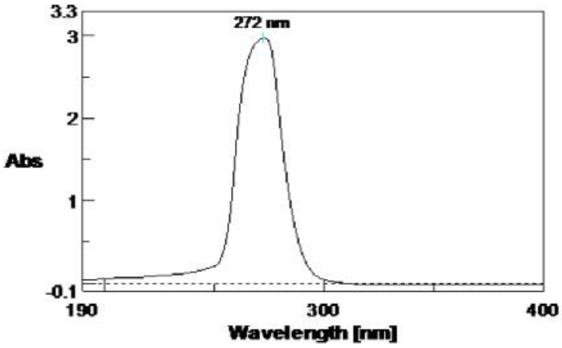


Fig.6. UV Spectrum of PBMA

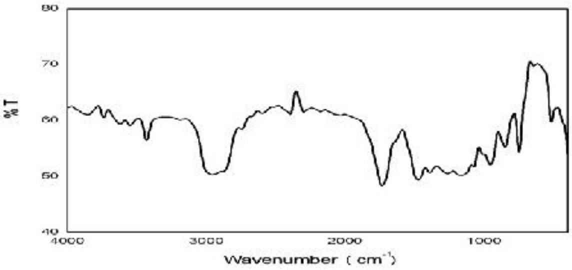


Fig.7. IR Spectrum of PBMA

^{1}H NMR Spectroscopy

In ^{1}HNMR spectrum (Fig.8), the peak at 2.5 ppm corresponds to the presence of proton of the ester group (Graybeal, Jack 1988) of the polymer. A peak at 3.9 ppm corresponds to the methylene group attached with the alkene group of the polymer (Kalsi 2002). Various peaks at 0.9 ppm, 1.4 ppm, 1.5 ppm and 1.9 ppm corresponds to the presence of various methylene and methyl protons of the butyl group present in the polymer (Kalsi (2002).

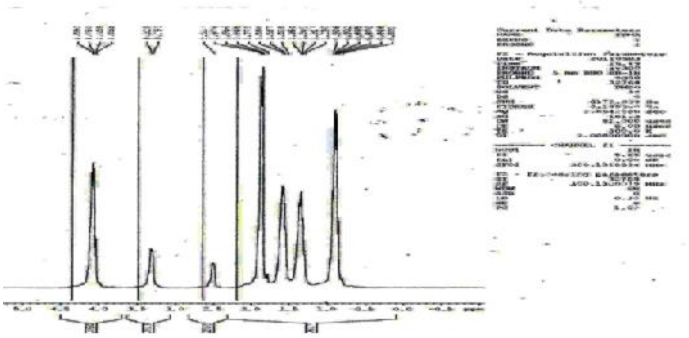


Fig.8. ^{1}H NMR Spectrum of PBMA

^{13}C NMR Spectroscopy

The ^{13}CNMR spectrum (Fig.9) shows a dominant peak at 40 ppm corresponds to the quaternary carbon atom of the polymer. (Graybeal, Jack 1988) A peak at 138 ppm corresponds to the presence of carbonyl carbon. The peaks at 14 ppm, 30 ppm, 60 ppm confirm the presence of methylene and methyl carbons of the butyl group present in the polymer (Kalsi 2002). The peaks at 126 ppm and 65 ppm corresponds to the methoxy carbon and methylene carbon present in the polymer (Kalsi 2002).

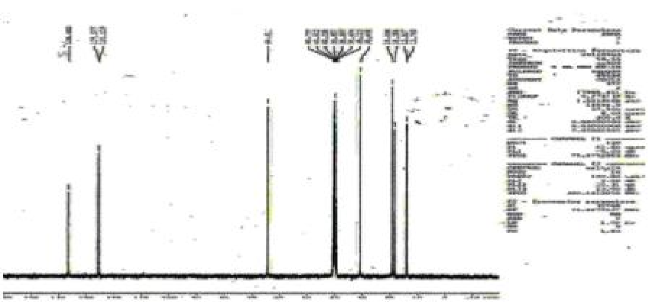


Fig.9. ^{13}C NMR Spectrum of PBMA

Viscosity measurements

The viscosity studies of the polymer which is useful to confirm the kinetics of the polymerization of BMA. The viscosity measurements of the obtained polymers can be done by using BROOKFIELD DV-II PRO VISCOMETER instrument (Table 7). The obtained results indicate that the growth as well as the viscosity of the polymers increases with increase of temperature.

Table 7. Viscosity measurements of the obtained polymers

Sample	Viscosity (centipoises)
PBMA1 (40°C)	-2.13
PBMA2 (50°C)	-2.92
PBMA3 (60°C)	-3.24

Conclusion

The kinetic features such as the rate of polymerization (Rp) of the free radical polymerization of butylmethacrylate (BMA) with the increasing concentrations of monomer, initiator, catalyst and temperature were studied. The acid strength and ionic strength of the medium do not show any appreciable effect in the Rp. The reaction rate increases was found to increase with increase in concentration of monomer (BMA), initiator (PDP) and phase transfer catalyst (HDTMAC). The reaction rate was found to be increase with increase in temperature also. The reaction order of the polymerization of BMA is in accordance with general rate law of free radical polymerization with respect to the concentration of initiator and catalyst. The order with respect to [Monomer], [PTC] and [PDP] are found to be 1, 0.5 and 0.5 respectively. The variation of acid strength and ionic strength was found to exert no significant change in the Rp in the present investigation. A mechanism for the polymerization of BMA has been proposed and it has been confirmed by the kinetic data obtained by the variation of [Monomer], [PTC] and [PDP]. In conclusion, it may be said that the potassium peroxy diphosphate (PDP) coupled with a PTC, hexadecyltrimethylcammoniumchloride, (HDTMAC) is a better initiator for the polymerization of butylmethacrylate in ethyl acetate-water bi phase system at 50 (±) 0.1^{0}C.

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