Synthesis of New Phase Transfer-Catalyzed Free Radical Polymerization of Ethyl Methacrylate: A Kinetic Study

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ABSTRACT: In this study, a new phase transfer catalyst has been synthesized and characterized, which is used for the study of kinetics and mechanism of the free radical polymerization of ethyl methacrylate. The reactions were carried out using peroxodisulfate as initiator in inert and unstirred condition at $60°C \pm 1°C$. The order with respect to monomer, initiator, and catalyst were found to be 1, 0.7, and 0.5, respectively. The rate of polymerization is independent of ionic strength and pH. Based on the results obtained, a mechanism has been proposed for the polymerization reactions. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 637–643, 2009

Key words: kinetics; mechanism; free-radical polymerization; ethyl methacrylate; phase transfer catalyst

INTRODUCTION

Phase transfer catalyst (PTC) relates to chemical reactions in which the reactants are in two separate phases such as in liquid–liquid, solid–liquid, and gas–liquid reactions. In such cases, the rates and yields are very often limited by the slow transport of reactants from one phase to another. The PTC does the work of extracting the reactive anions from the aqueous phase and transfers them to the organic phase containing the reactant. PTC is the most widely used method for solving the problem of the mutual insolubility of nonpolar and ionic compounds. PTC, preceeded by some early reports, has emerged since 1971 as a versatile technique and became a very fascinating field of chemistry. PTC has attracted tremendous attention since 1965 and has been applied to hundreds of reactions.

A wide variety of reactions have been examined, but most of the publications have dealt with alkylations and epoxidation. PTC is an efficient methodology for the synthesis of a variety of compounds, such as haloalkanes, alkenes, aliphatic nitro compounds, nitriles, azides, sulfides, pharmaceuticals, amino acids, pesticides, and polymers.[1] Quaternary ammonium salts and phosphonium salts are the most commonly used PTCs because of their relatively low cost and ready availability.[2] The catalytic methodology offers many significant advantages[1] over other methods, for example,

1. Acceleration of the rate under mild reaction conditions,
2. Use of inexpensive, recoverable, and nontoxic solvents,
3. Use of solvent-free reaction condition,
4. Use of inexpensive and commercially available catalysts,
5. Use of inexpensive inorganic bases for anion generation,
6. Improvement of yield and enantioselectivity of products, and
7. Use of continuous operations for large-scale industrial operations.

The first report on the phase transfer catalyst (PTC) for free radical polymerization was by Rasmussen and Smith.[3,4] They reported the polymerization of butyl acrylate with different crown ethers as PTCs and potassium peroxydisulfate as water-r soluble initiator. Jayakrishnan and Shah[5,6] studied the polymerization of acrylonitrile and methyl methacrylate using hexadecylpyridinium chloride as PTC in ethyl acetate–water medium.

In this work, the polymerization of the monomer-ethyl methacrylate in the presence of a PTC using potassium peroxydisulfate as initiator is studied. The reactions were carried out under inert condition at constant temperature of $60 \pm 1°C$. The results are discussed and a mechanism for polymerization has been proposed.

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EXPERIMENTAL

Dimethyl amine hydrochloride (AR grade SRL, Super Religare Laboratories Ltd., Mumbai, India),

paraformaldehyde (AR grade CDH, Central Drug House, New Delhi, India), and acetophenone (AR grade CDH, India) was used as received. The solvents cyclohexanone, ethanol, and methanol were distilled and used. Water employed was laboratory distilled. The monomer ethyl methacrylate was purified by usual procedure. The reaction tubes for the polymerization were long pyrex glass tubes with B-24 quick-fit sockets fitted with a provision for inlet and outlet for nitrogen gas. The polymerization reactions were carried out in an inert atmosphere at constant temperature of 60°C. The reaction mixture consists of aqueous and organic phases. The monomer in cyclohexanone is the organic phase. The catalyst, sodium bisulfate (for adjusting the ionic strength), and sulfuric acid (for maintaining $[H^+]$) were taken in the aqueous phase. When a calculated amount of peroxydisulfate was added to the reaction mixture, polymerization started and precipitate formed continuously. The reaction was arrested by pouring the reaction mixture into ice-cold methanol containing traces of hydroquinone.[7] The polymer formed was filtered quantitatively through a sintered crucible (IG-4), washed several times with double distilled water and methanol, and dried at 50–60°C in a vacuum oven to constant weight. The rate of polymerization (R_p) was determined gravimetrically.[8]

RESULTS AND DISCUSSION

A new PTC propiophenone benzyldimethylammonium chloride (PPBDMAC) has been synthesized, characterized, and used for the study of kinetics and mechanism of free radical polymerization of ethyl methacrylate. The reactions were carried out using peroxodisulfate as initiator in inert and unstirred condition at 60°C.

Synthesis of phase transfer catalyst—propiophenone benzyldimethylammonium chloride

The synthesis of the PTC involves two stages. In the first stage, a Mannich base that is dimethylamine-propiophenone hydrochloride has been prepared. Using this compound, the quaternary ammonium salt, PPBDMAC has been synthesized in the second stage.

Dimethylaminopropiophenone hydrochloride was prepared by refluxing dimethyl amine hydrochloride (0.326 mol), paraformaldehyde (0.33 mol), and acetophenone (0.25 mol) along with 40 mL of 95% ethanol containing 0.5 mL of concentrated hydrochloric acid for 2 h in a round-bottomed flask. Dimethylaminopropiophenone hydrochloride was diluted in water and neutralized slowly by adding 5% solution of so-
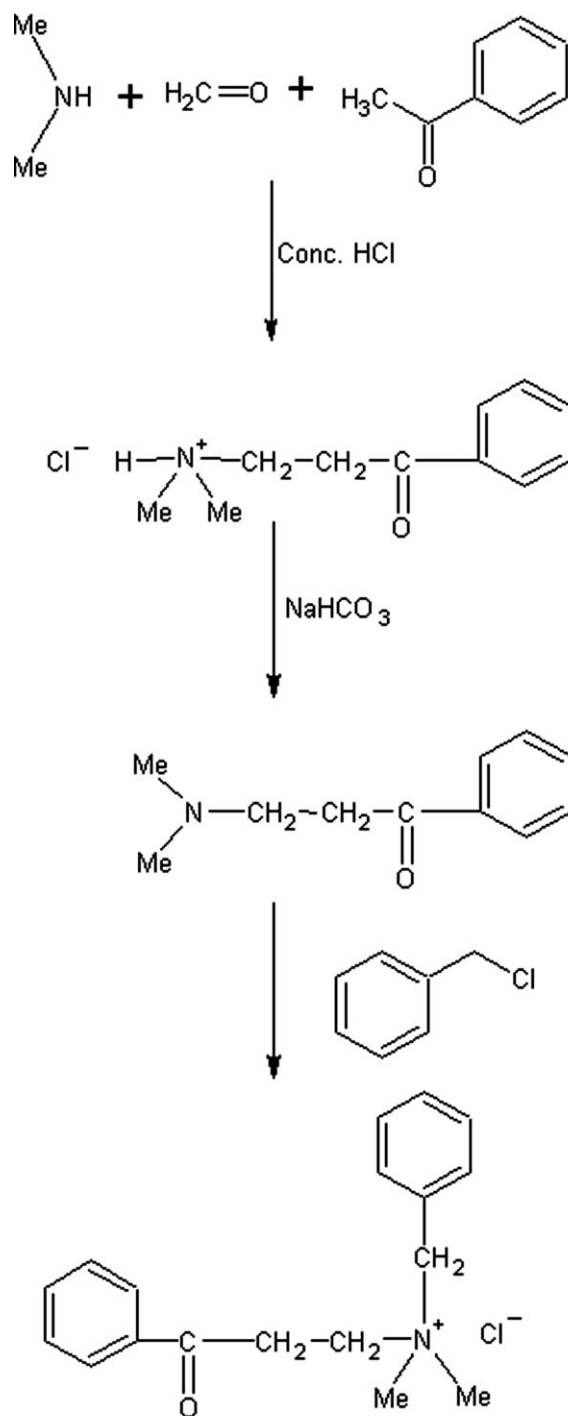
Figure 1 Propiophenone benzyldimethylammonium chloride.

dium bicarbonate until effervescence ceased. The liberated amine was then extracted with ether by using a 250-mL separating funnel. The resulting amine was then quaternized by adding benzyl chloride (0.035 mL) under cold condition. The salt obtained was purified by recrystallized with alcohol–acetone mixture.
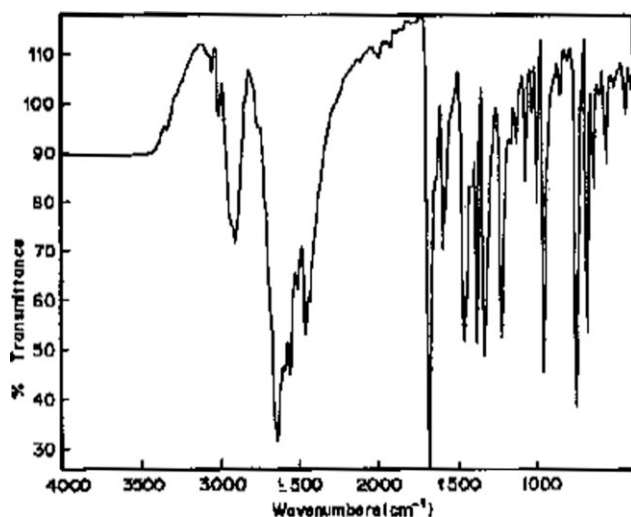
Figure 2 Infrared spectrum of propiophenone benzyldimethylammonium chloride.

Characterization of phase transfer catalyst

IR spectral data

The IR spectrum of the PTC was obtained from Nicolet-Impact 400 MHz spectrometer. The aromatic C—H stretching mode appears at 3010 cm^{-1}. The aliphatic C—H modes have produced a sharp peak just below 3000 cm^{-1}. The multiple combination bands characteristic of quaternary ammonium salts is positional between 2410 and 2700 cm^{-1}. The sharp peaks at 1690 cm^{-1} are due to carbonyl stretching. Aromatic ring skeletal vibrations are positioned at 1600, 1500, and 1450 cm^{-1}. Aliphatic C—H bending modes appear at 1375 and 1450 cm^{-1}. The presence of monosubstitution on aromatic ring is evident by the two sharp peaks appearing at 690 and 750 cm^{-1}. The peaks at 1210 cm^{-1} are due to C—N stretch (Figs. 1 and 2)

^{1}H-NMR spectral data

The 300 MHz ^{1}H-NMR spectrum of the PTC was taken from the Brucker Instrument. Aromatic protons of benzoyl and benzyl groups are well resolved and positioned at 7.75 and 7.2–7.4 ppm, respectively. Methylene protons of —CO—CH$_2$ and —N—CH$_2$— groups produced signals at 1.77 and 1.79 ppm, respectively. The signals due to proton of —N—(CH$_3$)$_2$ group and methylene protons of benzyl group got mixed and produced a single signal at 2.67 ppm (Fig. 3).

^{13}C-NMR spectral data

The 300 MHz ^{13}C-NMR proton decoupled spectrum of the catalyst was taken from the Brucker Instrument. The carbonyl carbon produced its signal at
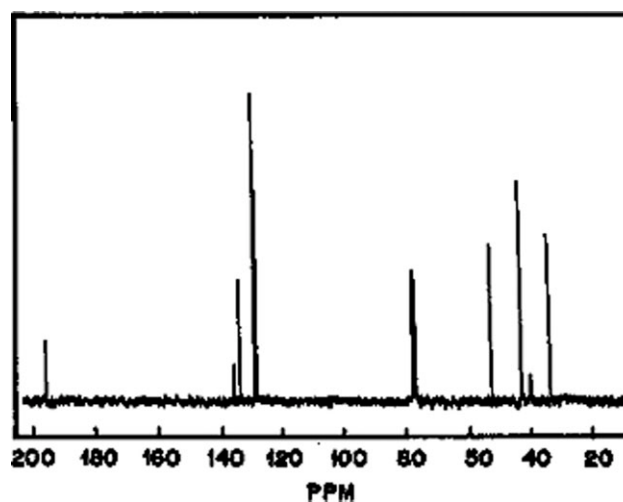

Figure 3 ^{1}H-NMR spectrum of propiophenone benzyldimethylammonium chloride.

195.7 ppm. The aromatic carbons produce signals between 128 and 135.5 ppm. The triplets at 78 ppm are due to CDCl$_3$. The signals of N—CH$_2$—, —CO—CH$_2$, and N(CH$_3$)$_2$ carbons are placed at 52.5, 43, and 33.5 ppm (Fig. 4), respectively.

Phase transfer-catalyzed polymerization

The PTC-assisted free radical polymerization using water-soluble peroxodisulfate as initiator has become popular in recent years in contrast to the conventional polymerization techniques using organic soluble initiators like AIBN and benzoyl peroxide for the following reasons:

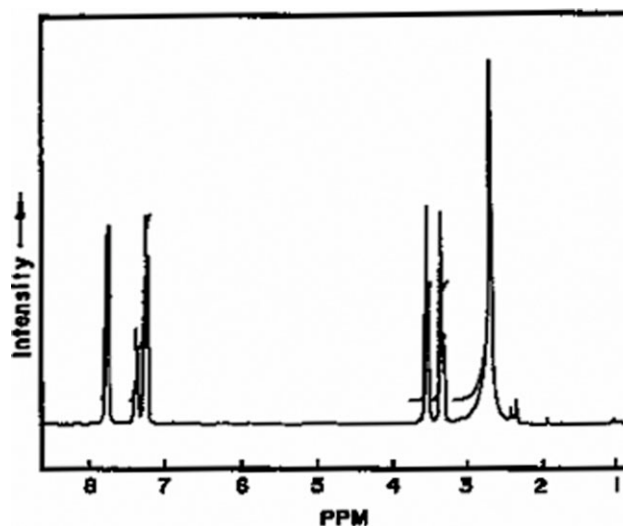1. High rate of polymerization under mild experimental conditions.

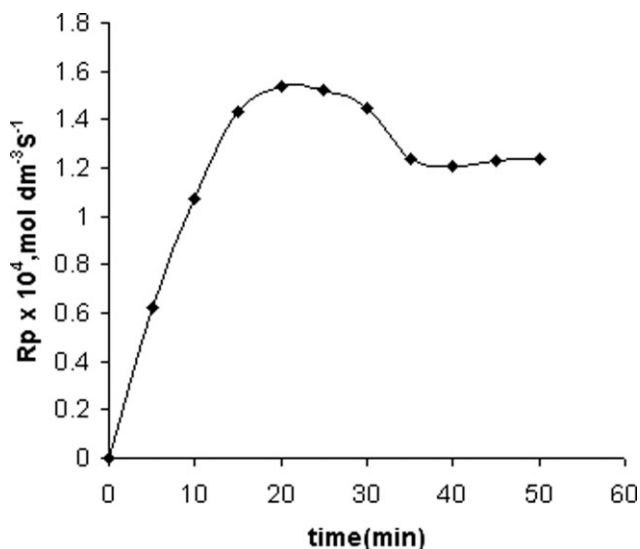**Figure 4** ^{13}C-NMR spectrum of propiophenone benzyldimethylammonium chloride.

Figure 5 EMA-PPBDMAC-$K_2S_2O_8$ system. Steady-state rate of polymerization.

2. Good mechanical properties like shearing strength of the polymers.
3. High-molecular weight polymers can be prepared even with the free radical mechanism.
4. The polydispersity value is constant even up to high polymer conversion.

Kinetics of polymerization of ethyl methacrylate

The polymerization of ethyl methacrylate initiated by Peroxodi sulfate-PTC in cyclohexanone/water biphase is studied under different exper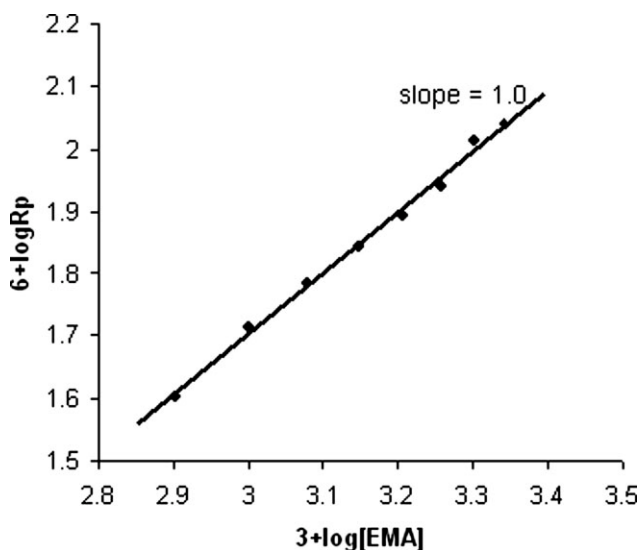imental conditions to evaluate the various parameters, which influence the polymerization reactions. The effect of alkyl chain length on reactivity of the monomer in the PTC-assisted free radical polymerization is also studied.

Steady-state rate of polymerization

The steady-state rate of polymerization was first arrived by determining R_p at different time intervals and it was found to be 35 min. The reaction time was fixed at 35 min to carry out the experiments with variation in other parameters (Figs. 5 and 6).[9]

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

The effect of monomer concentration on the rate of polymerization was studied by carrying out the reaction at varying monomer concentration in the range of 0.8–2.2 mol dm^{-3} at fixed concentration of potassium peroxydisulfate, catalyst, ionic strength, and pH. The rate of polymerization increases with increasing monomer concentration, and the order of the reaction was obtained from a plot of log R_p versus log [EMA] and the value was found to be unity. A plot of R_p versus [EMA]^1 is linear passing through the origin (Fig. 7).[10,11]

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

By keeping other parameters constant, the effect of concentration of potassium peroxydisulfate on the rate of polymerization of ethyl methacrylate was studied by varying the concentration of initiator in
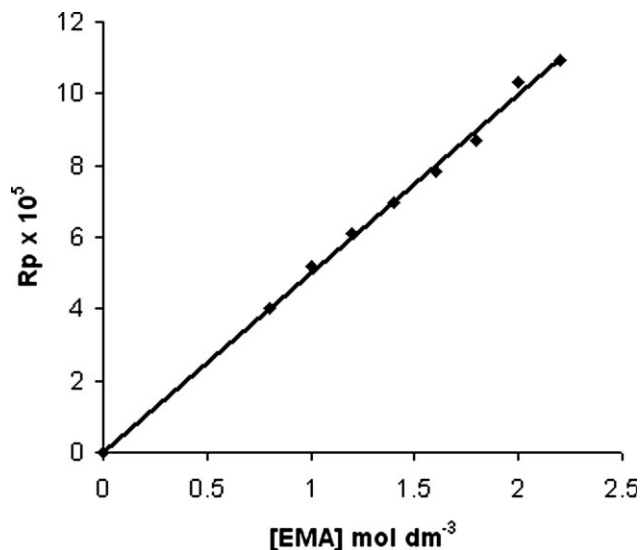

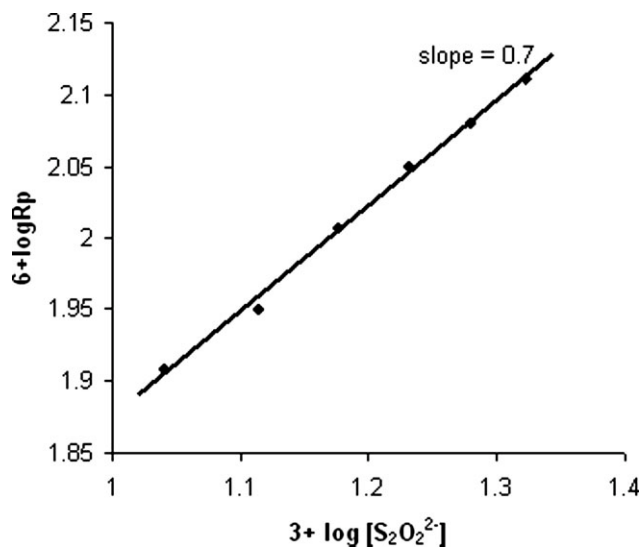**Figure 6** EMA-PPBDMAC-$K_2S_2O_8$ system. Variation of [Monomer].

Figure 7 EMA-PPBDMAC-$K_2S_2O_8$ system. Variation of [EMA].

Figure 8 EMA-PPBDMAC-$K_2S_2O_8$ system. Variation of $[K_2S_2O_8]$.

Figure 10 EMA-PPBDMAC-$K_2S_2O_8$ system. Variation of [PPBDMAC].

the range 0.011–0.021 mol dm^{-3}. Rate of polymerization was found to increase with increasing concentration of initiator in the system. From the plot of log R_p versus log $[K_2S_2O_8]$, the slope is almost equal to 0.7. As expected a plot of R_p versus $[K_2S_2O_8]^{0.7}$ is linear passing through the origin supporting the above deduction (Figs. 8 and 9).

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

The effect of concentration of the PTC on the polymerization rate was studied by varying the concentration in the range 0.006–0.016 mol dm^{-3}, keeping other parameters constant. Rate of polymerization

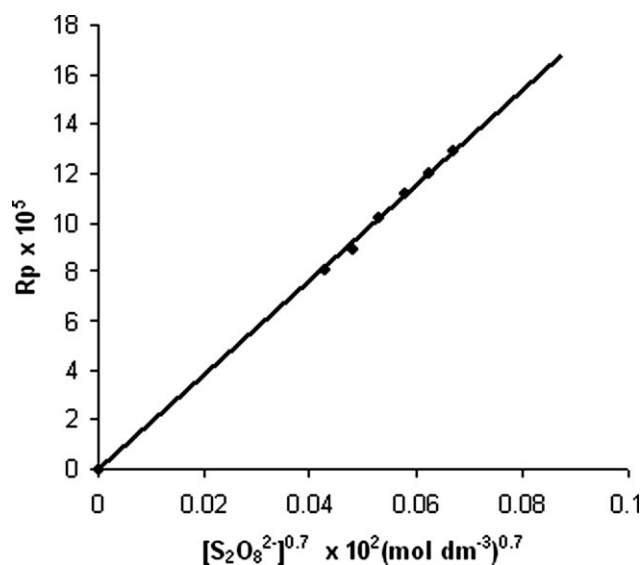was found to increase with increase in the concentration of catalyst. The order with respect to the concentration of the catalyst is found to be around 0.5 from a plot of log R_p versus log [PTC]. A plot of R_p versus $[PTC]^{0.5}$ is found to be linear passing through the origin confirming this result. It has also been observed that in the absence of PTC, no polymerization occurred even after several hours (Figs. 10 and 11).[12]

Effect of variation of volume fraction of aqueous phase on the rate of polymerization (R_p)

To study the effect of variation in the volume fraction of aqueous phase on the rate of polymerization, the reaction was conducted by varying other
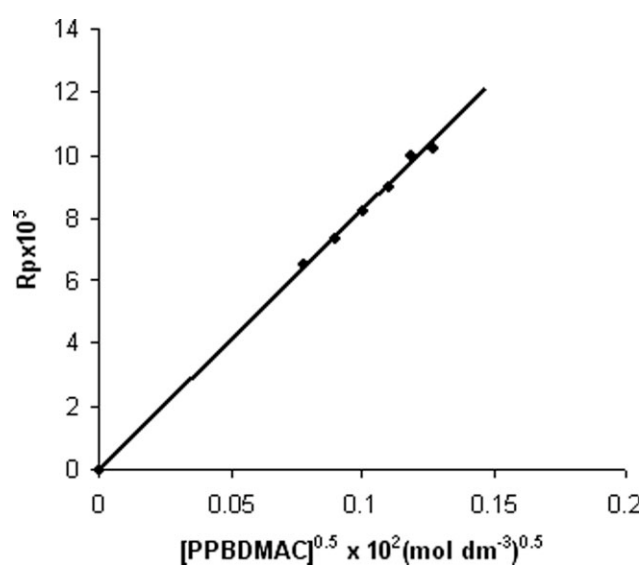

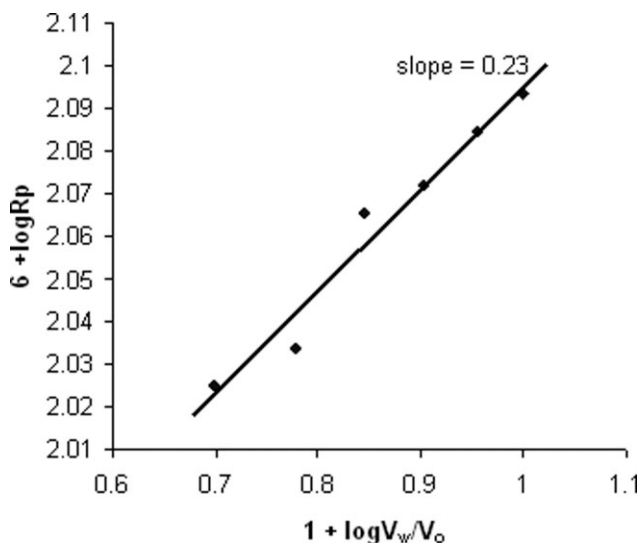**Figure 9** EMA-PPBDMAC-$K_2S_2O_8$ system. Variation of $[K_2S_2O_8]$.

Figure 11 EMA-PPBDMAC-$K_2S_2O_8$ system. Variation of [PPBDMAC].

Figure 12 EMA-PPBDMAC-$K_2S_2O_8$ system. Variation of aqueous phase volume.

parameters. The ratio of volumes of two phases V_w/V_o was varied in the range 0.5–1. It is observed that there is a slight increase in the rate of polymerization with an increase in V_w/V_o ratio (Fig. 12).[13]

Effect of solvent on the rate of polymerization (R_p)

The effect of solvent on the rate of polymerization was examined by carrying out the polymerization reaction for ethyl methacrylate in three different solvents such as cyclohexane, ethyl acetate, and cyclohexanone having the dielectric constants 2.5, 6.5, and 18.3, respectively. It is found that the R_p decreased in the following order:

cyclohexanone > ethyl acetate > cyclohexane (Table I).

The decrease in the rate of polymerization may be due to the increase in the polarity of the organic medium, which facilitates greater transfer of peroxydisulfate to the organic phase.
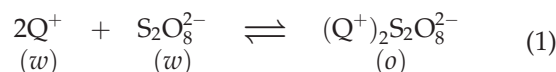
Effect of variation of temperature on the rate of polymerization (R_p)

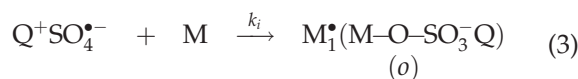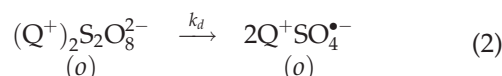The effect of variation of temperature in the range of 50–60°C on the polymerization was studied by keeping other variables constant. The rate of polymerization increases with the increase in temperature. From the slope of the Arrhenius plot of log R_p versus $1/T$, the activation energy values for the polymerization reactions were calculated. The thermodynamic parameters such as entropy of activation, enthalpy of activation, and free energy of activation have been calculated from the value of activation energy (Fig. 13).[14]

Mechanism and rate law

(a) Phase transfer

$$\underset{(w)}{2Q^+} + \underset{(w)}{S_2O_8^{2-}} \rightleftharpoons \underset{(o)}{(Q^+)_2 S_2 O_8^{2-}} \tag{1}$$

(b) Initiation

$$\underset{(o)}{(Q^+)_2 S_2 O_8^{2-}} \xrightarrow{k_d} \underset{(o)}{2Q^+ SO_4^{\bullet-}} \tag{2}$$

$$Q^+SO_4^{\bullet-} + M \xrightarrow{k_i} \underset{(o)}{M_1^\bullet (M-O-SO_3^- Q)} \tag{3}$$

(c) Propagation

$$M_1^\bullet + M \xrightarrow{k_p} M_2^\bullet \tag{4}$$

$$M_{n-1}^\bullet + M \xrightarrow{k_p} M_n^\bullet \tag{5}$$

(d) Termination

$$2M_n^\bullet \xrightarrow{k_t} \text{polymer} \tag{6}$$

The subscript (w) and (o) refer to water phase and organic phase, respectively. Q refers to the catalyst. This mechanism involves the formation of quaternary ammonium peroxydisulfate complex $[(Q^+)_2 S_2 O_8^{2-}]$ 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 derived as follows:

TABLE I
Dependence of R_p on Solvent Polarity

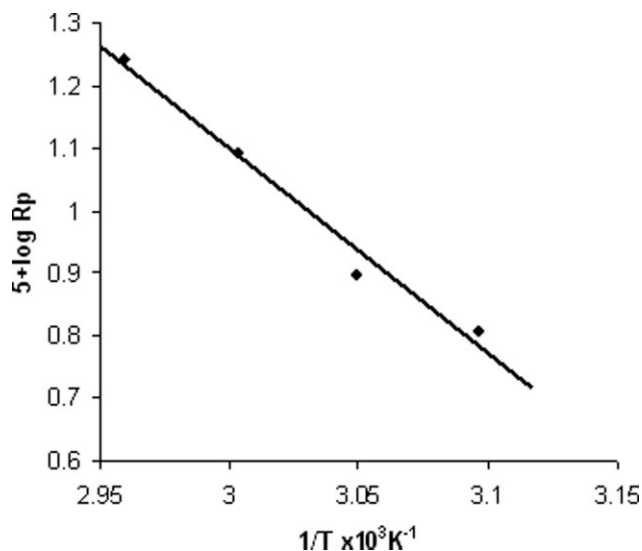|	$R_p \times 10^5$, mol dm^{-3} S^{-1}		
Experimental conditions	Cyclohexane ($\varepsilon = 2.5$)	Ethyl acetate ($\varepsilon = 6.5$)	Cyclohexanone ($\varepsilon = 18.3$)
[EMA] = 2.5 mol dm^{-3} [$K_2S_2O_8$] = 2.0 × 10^{-2} mol dm^{-3} [PPBDMAC] = 2.0 × 10^{-2} mol dm^{-3} Temperature = 60°C	6.85	8.2	12.40

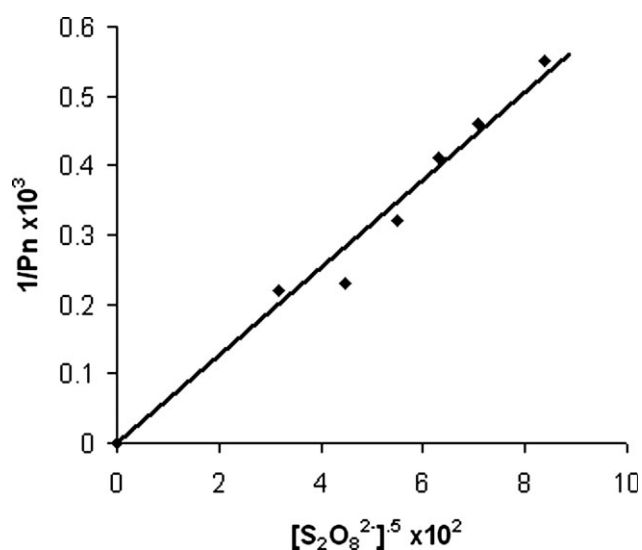**Figure 13** EMA-PPBDMAC-$K_2S_2O_8$ system. Arrhenius plot.

Figure 14 EMA-PPBDMAC-$K_2S_2O_8$ system. Dependence of degree of polymerization on [$K_2S_2O_8$].

$$R_p = k_p \left(\frac{k_d K}{k_t} \right)^{1/2} \frac{[M]\,[S_2O_8^{2-}]^{0.7}\,[Q^+]_{total}}{1 + K[Q^+]_w \quad [S_2O_8^{2-}]_w} \tag{7}$$

This expression satisfactorily explains all the experimental results and observations.

The degree of polymerization of the polymer was evaluated from the intrinsic viscosity data obtained from the viscosity measurements of polymer with varying concentrations of potassium peroxodisulfate.[14] The degree of polymerization decreases with increasing initiator concentration. A plot of $1/P_n$ versus $[K_2S_2O_8]^{1/2}$ gives a straight line. This provides

TABLE II
Thermodynamic Parameters

Monomer	E_a (kcal mol^{-1})	$\Delta S^{\#}$ (eu)	$\Delta H^{\#}$ (kcal mol^{-1})	$\Delta G^{\#}$ (kcal mol^{-1})
EMA	14.99	−31.64	14.33	24.76

additional evidence for the proposed mechanism (Fig. 14).

CONCLUSION

In this work, a quaternary ammonium salt, which is one of the potential PTCs, has been synthesized, characterized and used for the study of kinetics and mechanism of the free radical polymerization of ethyl methacrylate. The polymerization reactions were carried out under inert and unstirred conditions at constant temperature of 60°C in cyclohexanone/water biphase media using $K_2S_2O_8$ as the water-soluble initiator.

The dependence of the rate of polymerization on various experimental conditions such as different concentrations of monomers, initiator, catalyst and different ionic strength, temperature, and volume fraction of aqueous phase were discussed. The order with respect to monomer, initiator, and catalyst were found to be 1.0, 0.7, and 0.5, respectively.

Activation energy for the polymerization of the monomer is calculated from the slope of log R_p versus $1/T$ in the temperature range 50–60°C. The other thermodynamic parameters were also calculated for the monomer (Table II). Based on the kinetic results, suitable mechanism has been proposed.

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