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RESEARCH ARTICLE

KINETICS OF FREE RADICAL POLYMERIZATION OF METHYLACRYLATE INITIATED BY POTASSIUM PEROXYDISULFATE AND CETYLPYRIDINIUM CHLORIDE SYSTEM

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ABSTRACT

Kinetics of phase transfer catalyst (PTC) assisted polymerization of Methyl acrylate (MA) initiated by potassium Peroxydisulfate ($K_2S_2O_8$) – cetylpyridinium chloride (CPC) system was investigated in ethyl acetate/water system at 60ºC under N_2 atmosphere and unstirred condition. The effect of varying the concentrations of MA, $K_2S_2O_8$, CPC, $H^{+,}$ and ionic strength on Rp were studied. From the study, reaction orders with respect to MA, $K_2S_2O_8$ and CPC were found to be 1.5, 0.5 and 1. Thermodynamic parameters such as overall activation energy (E_a), entropy of activation ($\Delta S^{\#}$), enthalpy of activation ($\Delta H^{\#}$) and free energy of activation ($\Delta G^{\#}$) were calculated by conducting the reaction at different temperatures in the range 50-60ºC. Rate of the reaction was found to be unaffected by a change in the acid strength and ionic strength of the reaction medium. To account for the experimental observations, the most probable mechanism has been proposed and the rate expression was derived from it.

INTRODUCTION

Phase transfer catalysis is a method which allows carrying out a reaction between a substrate solublein an organic solvent and an ionic reagent insoluble in this solvent, by using a phase transfer agent.Though the first report on phase transfer catalysis had appeared in 1965, the method has beenemployed by several research groups only after 1969 (Makosza and Serafinowa, 1965; Makosza and Serafinowa, 1965; Gibson and Hosking, 1965; Makosza, 1969; Weber and Gokel, 1978; Starks and Liotta, 1978 and Keller, 1979). Owing to its simplicity and low cost of mostof the phase transfer catalysts [PTC], the method has found universal adoption. Studies on the kineticsof polymerization of vinyl monomers were carried out by many workers under differentconditions (Thajudeen *et al*., 2008; JamalAhamed *et al*., 2012; Vajjiravel and Umapathy, 2008; Vajjiravel and Umapathy, 2010 and Vajjiravel and Umapathy, 2011). Phase transfer catalysts assisted free radical polymerization of olefinic monomers was reported forthe first time by Rasmussen and Smith in 1981 (Rsmussen and Smith, 1981; Rsmussen and Smith, 1981; Rsmussen and Smith, 1982). They investigated the peroxydisulfate initiatedpolymerization of butyl acrylate using various crown ethers and quaternary ammonium salts as phasetransfer catalysts in ethyl acetate/water two phase systems. It was shown that using phase transfercatalysts, peroxydisulfate can be phase transferred into a variety of solvents, including hydrocarbon solvents. Potassium peroxomonosulfate was shown for the first time by Kennedy *et al* to initiate vinylpolymerization. PMS in combination with suitable reducing agents produces free radicals, viz, $SO4^{\bullet -}$and $OH^{\bullet}$ responsible for initiation of polymerization. Polymerization of acrylonitrile was shown to beinitiated by PMS in the presence of Ag(I), Mn(II), Cu(II) – salicylaldehyde and α-naphthol-chelatecomplex of Cu(II). Thangarag *et al.* (2014) Phase transfer catalysis, peroxydiphosphate as an initiator, kinetics and mechanism, acrylonitrile, spectral studies. Shabeer *et al*. (2012) investigated the kinetics of Phase transfer catalysis, kinetics of polymerization, acrylonitrile, potassium peroxomonosulfate, cetylpyridinium chloride.

MATERIALS AND METHODS

Polymerization studies were carried out in long pyrex tubes [4 cm x 20 cm] of about 80 ml capacitywith B-24 quickfit socket fitted with B-24 cone with a provision for inlet and outlet terminals in orderto isolate the reaction mixture from the atmospheric oxygen. All the experiments were conducted in

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athermostat bath of 20 litre capacity. Experiments were carried out in the temperature range 50-60°C.Nitrogen gas used for deaeration was freed from the traces of oxygen and other impurities by passingthrough four vertical glass tubes containing separately.

- Fieser's solution,
- Lead acetate solution,
- Potassium hydroxide solution and
- Distilled water.

A constant deaeration time was used for allthe experiments. Double distilled water was used throughout the experiment for the preparation ofreagents and solutions. The monomer methyl acrylate, cetylpyridinium chloride (Spectrochem), potassium peroxydisulfate known as OXONE (Merck,Germany), sulfuric acid (Qualigens) and potassium sulfate (SD fine) were used as received.

Polymerization technique

Polymerization reactions were carried out in the reaction vessels thermo stated at the desired temperature. A known amount of monomer, cetylpyridinium chloride, sulfuric acid and potassium sulfate were taken in the reaction tube and flushed with purified nitrogen gas for about 30 minutes toensure an inert atmosphere. A calculated amount of desecrated peroxydisulfate solution thermo stated at the experimental temperature was added to the reaction mixture and simultaneously a stopwatch was started. The reaction tubes were then carefully sealed by rubber gaskets to ensure an inertatmosphere. The reaction was arrested by blowing air inside the tube and keeping the reaction vessel in ice cold water for some time. The polymer was filtered out quantitatively through a crucible (G-3), washed several times with double distilled water and dried at 50-60°C in a vacuum oven to a constant weight. The rate of polymerization was computed from the weight of the polymer formed, using the following relation

Rp = 1000 W/VtM

Where,

W = weight of the polymer
V = total volume of the reaction mixtures
t = reaction time in seconds
M = molecular weight of the monomer

By separate experiments it was confirmed that neither PDS nor CPC alone initiated polymerization under the experimental conditions employed.

Analysis of the results

In order to estimate the limits of consistency in the results, duplicate experiments were carried out under identical conditions and it was found that the Rp values were subjected to the error limits of ±2%. The accuracy of the results was tested by the method of least squares.

RESULTS AND DISCUSSION

The present investigation deals with the kinetics and mechanism of phase transfer catalyst assisted polymerization of Methyl acrylate initiated by cetylpyridinium chloride $K_2S_20_8$ initiator system. Thepolymerization reactions were carried out in ethyl acetate-water two phase systems under nitrogenatmosphere and unstirred conditions at 60°C. The dependence of rate of polymerization Rp on [MA],[CPC], $[K_2S_20_8]$, $[H^+]$, ionic strength and temperature was studied. The polymerization of MA with the CPC - $K_2S_20_8$ initiator system proceeded fast, but in the absenceof either CPC or $K_2S_20_8$ the polymer was not detected. The results obtained in this investigation arepresented in the form of Figures 1 to 6

Steady State Rate of Polymerization: Polymerization reactions were carried out at different time intervals at fixed concentrations of MA, CPC, and H^+ and ionic strength to arrive at the steady state rate of polymerization. It has been found that at first the polymerization rate increased sharply with time, then decreases and finally attains a constant value. Steady state rate of polymerization was found to be attained at about 3 hours (Fig.1). To study the effects of various reaction parameters on the rate of polymerization, the polymerization was conducted for duration of 3 hours.

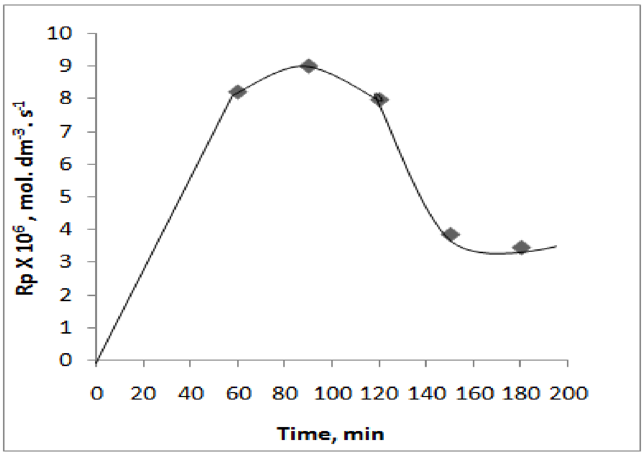

Fig . 1. Steady State Rate of Polymerization

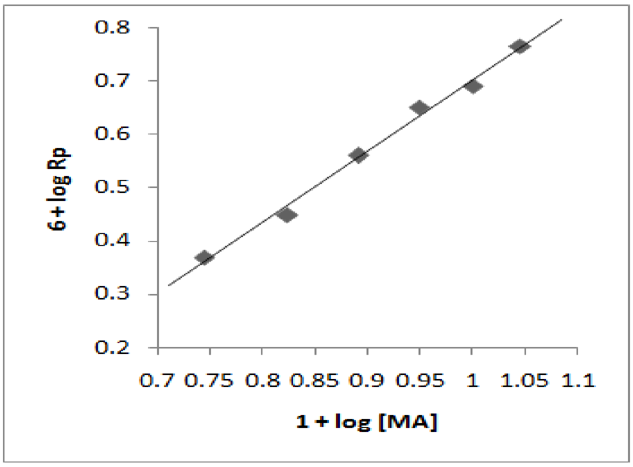

Fig .2. Dependence of [MA] ON Rp

Effect of [MA] on Rp

To find the effect of [MA] on Rp the concentration of MA was varied in the range of 0.5552- 1.1104 mol.dm^{-3} at fixed concentration of other components. Rp was found to increase with increase of [MA]. The slope $K_2S_20_8$of the straight line obtained in the plot of log RpVs log [MA] is equal to 1.5 (Fig. 2.). The reaction order greater than unity with respect to monomer is a common observation in the polymerization of MA.A reaction order greater than unity with respect to the concentration of the monomer may be ascribed to the dependence of initiation rate on monomer concentration, primary radical termination or the phenomenon of the gel-effect or occlusion. Since in the present investigation, the order with respect to initiator is found to be 0.5, the possibility of primary radical termination can be ruled out. Moreover, all the reactions are carried out at 60°C and at this high temperature the incidence of occlusion can be discounted. The half order dependence of reaction rate on initiator concentration eliminates the possibility of gel-effect. Hence, the dependence of the initiation rate on the concentration of the monomer could have contributed to the monomer order of 1.5 observed in this study.

Effect of [PDS] on Rp

The effect of varying the [$K_2S_20_8$] on Rp was examined by varying [$K_2S_20_8$] in the range of 2.5 x 10^{-3} – 5.0 x 10^{-3} mol.dm^{-3} at fixed [MA], [CPC], [H$^+$] and ionic strength. Rp increases with increase in the [$K_2S_20_8$]. A plot of log RpVs log [$K_2S_20_8$] is linear with a slope of 0.5 indicating the half order dependence of Rp on [$K_2S_20_8$] (Fig.3.). The half order dependence of Rp on initiator concentration indicates that the termination is bimolecular.

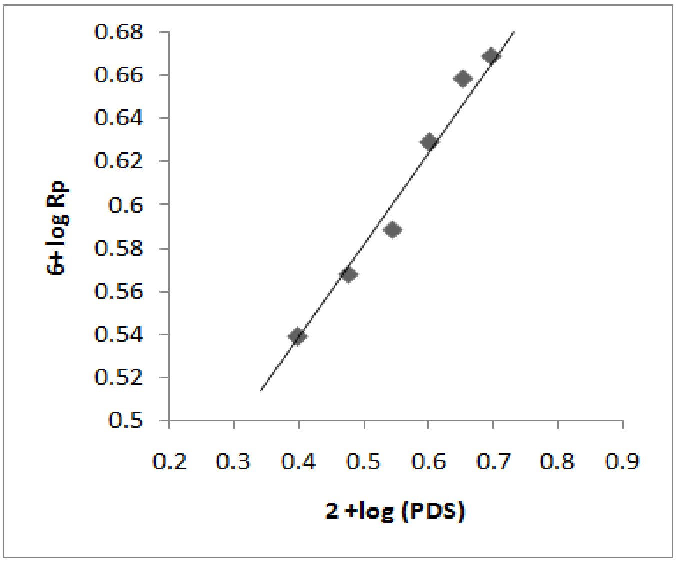

Fig . 3. Dependence of [PDS] ON R_p

Effect of [CPC] on Rp

It has been observed that increase of [CPC] increases the values of Rp in the concentration range employed 2.5 x 10^{-3} – 5.0 x 10^{-3} mol.dm^{-3}. From the slope of bilogarithmic plot of RpVs [CPC], the rate exponent with respect to [CPC] was found to be one (Fig.4)

Effect on temperature on Rp

Polymerization was carried out at different temperatures viz. 328, 333.and 338. K at definite concentrations of MA, $K_2S_20_8$, CPC, H$^+$ and ionic strength. The rate of polymerization increases with temperature. The activation energy for the overall rate of polymerization has been computed from the Arrhenius plot of log RpVs 1/T (Fig.5.) and was found to be 81.1 kJ.mol^{-1}. The other thermodynamic parameters such as $\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ have also been calculated, from the Eyring plot of log(Rp/T) Vs 1/T (Fig. 6) and was found to be 59.65 kJ.mol-1, 78.3 kJ.mol^{-1} and -55.98 EU respectively.

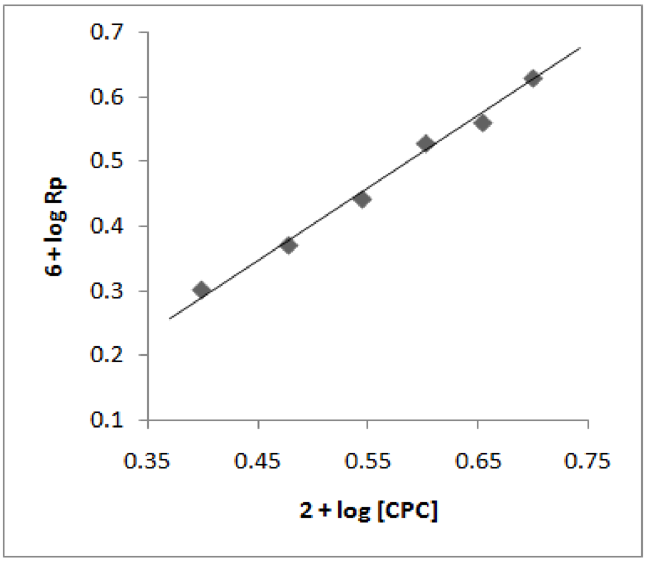

Fig .4. Dependence of [CPC] ON R_p

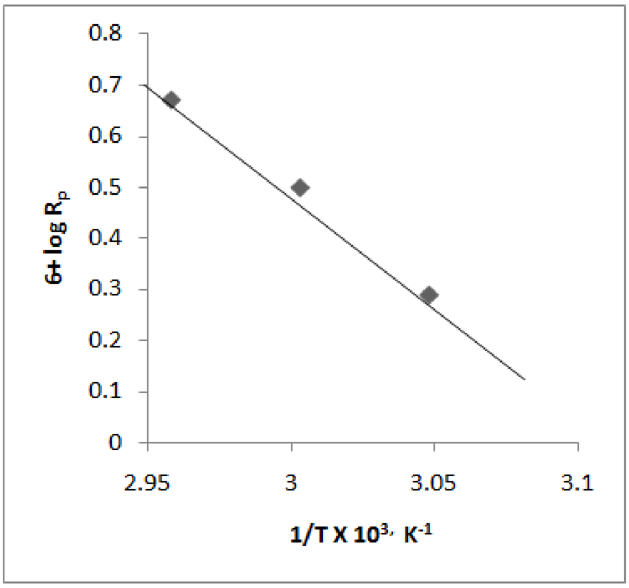

Fig. 5. Arrhenius Plot

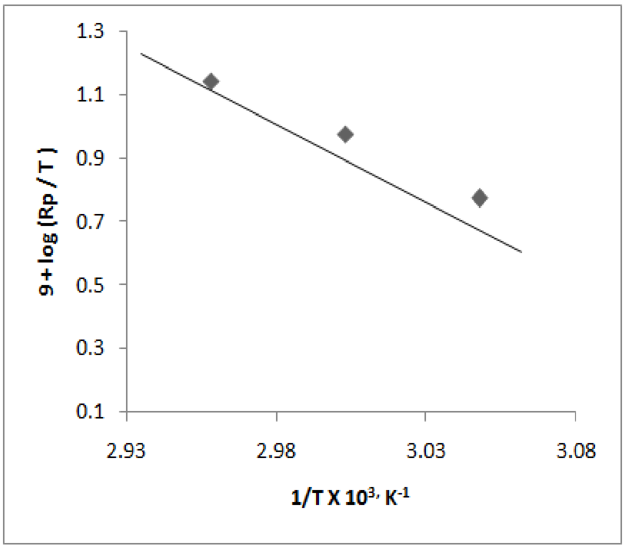

Fig .6 Eyring Plot

Effect of [H+] on Rp

The polymerization reaction was carried out employing different concentrations of acid in the range 0.16-0.26 mol.dm^{-3} at fixed concentrations of MA, PDS, CPC and at a constant ionic strength. Rp was found to be almost independent of variation in the acid strength in the range employed in this experiment.

Effect of ionic strength on Rp

To find out the effect of ionic strength on Rp the ionic strength of the reaction mixture was varied from 0.52 to 0.72 mol.dm^{-3} keeping the concentrations of other constituents of the reaction mixture constant. It has been observed that Rp is unaffected by a variation in the ionic strength of aqueous phase.

REACTION MECHANISM AND RATE LAW

The following salient features are observed in the present kinetic investigation of the polymerization of Methyl acrylate initiated by $K_2S_20_8$,- CPC catalyst system

- The reaction exponent with respect to [MA] = 1.5
- The reaction exponent with respect to [PDS] = 0.5
- The reaction exponent with respect to [CPC] = 1.0
- Rp is independent of [H$^+$] and ionic strength of the medium.

In the polymerization of MA initiated by the $K_2S_20_8$ – CPC catalyst system conducted under unstirred conditions employing equal volumes of aqueous and organic phases (Vw/Vo=1), the obtained results indicate the following notable points:

- The mechanism involves the transfer of monovalent peroxydisulfate ion from the Aqueous phase to monomer containing organic phase facilitated by the quaternary Ammonium salt, cetylpyridinium chloride (CPC).
- The observation of more than unity for monomer exponent indicates the participation of monomer in the radical forming process, i.e., monomer induced decomposition of ion-pairedperoxomonosulfate anion (Q^+ $K_2S_20_8$).

From the aforementioned points, it is clear that the mechanism involves the decomposition of the ion pair cetylpyridiniumperoxydisulfate (Q^+ $K_2S_20_8$) induced by the monomer molecule producing sulfate ion radicals, which exist in the form $Q^+SO_4^{\bullet -}$.

The initiation is followed by the usual propagation steps with bimolecular reaction of two polymer chains as the termination step. Based on these considerations the mechanism is given as follows:

Mechanism

(a) Phase Transfer

$$2Q^+_{(w)} + S_20_8{}^{2-}{}_{(w)} \overset{K}{\rightleftharpoons} (Q^+)_2\, S_20_8{}^{2-}{}_{(o)} \qquad (1)$$

(b) Initiation

$$(Q^+)_2S_20_8{}^{2-}{}_{(o)} + M_{(o)} \xrightarrow{k_d} M_1{}^{\bullet}{}_{(o)} + 2Q^+SO_4{}^{\bullet -}{}_{(o)} \qquad (2)$$

$$Q^+\, S0_4{}^{\bullet -}{}_{(o)} + M_{(o)} \xrightarrow{k_i} M_1{}^{\bullet}{}_{(o)} \qquad (3)$$

(c) Propagation

$$M_1{}^{\bullet} + M \xrightarrow{k_p} M_2{}^{\bullet} \qquad (4)$$

$$M^{\bullet}{}_{n-1} + M \xrightarrow{k_p} M_n{}^{\bullet} \qquad (5)$$

(d) Termination

$$2M_n{}^{\bullet} \xrightarrow{k_t} \textbf{Polymer} \qquad (6)$$

The subscripts (o) and (w) refer to the organic and aqueous phases respectively. Q refers to the phase transfer catalyst (CPC).

Applying the general principles of free radical polymerization and stationary state hypothesis to the radical species, the rate law for the mechanism can be derived.

$$R_p = k_p \frac{[k_d K]^{1/2} [M]^{3/2} [S_2O_8^{2-}]^{1/2} [Q^+]_{Total}}{[k_t]^{1/2} \quad 1 + K [Q^+] [S_2O_8^{2-}]_w}$$

The above derived expression satisfactorily explains the experimental observations.

Conclusion

The kinetics of the radical polymerization of Methyl acrylate was investigated using $K_2S_20_8$ as the initiator and cetylpyridinium chloride as the phase transfer catalyst in ethyl acetate/water biphase system at 60 ±1ºC under nitrogen atmosphere. Increase in the rate of polymerization (Rp**)** was observed with increasing concentration of monomer, initiator and catalyst. The acid and ionic strength of the medium did not show any appreciable effect on the Rp. The reaction rate increases with increasing temperature. The reaction orders with respect to monomer, initiator and catalyst were found to be 1.5, 0.5 and 1 respectively. Based on the results obtained a suitable kinetic scheme has been proposed.

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