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Kinetics of Free Radical Polymerization of Methylacrylate Initiated by Potassium Peroxomonosulphate and Tetrabutyl Phosphonium Chloride

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In present studies, the systematic study of kinetics and mechanism of phase-transfer catalyzed free radical polymerization of methylacrylate (MA) water-soluble initiator potassium peroxomonosulphate (PMS) coupled with tetrabutyl phosphonium chloride (TBPC) catalyst system in ethyl acetate/water bi-phase in the temperature range 45-55°C at fixed pH and ionic strength is reported. The rate of polymerization increases with an increase in concentration of MA, PMS and phase-transfer catalyst, *viz.*, tetrabutyl phosphonium chloride. It was observed that the rate of polymerization (Rp) is proportional to $[MA]^{1.0}$, $[KHSO_5^-]^{0.5}$ and $[TBPC]^{0.5}$. A suitable kinetic scheme has been proposed to account for the experimental observations and its significance was discussed.

Key Words: Kinetics of polymerization, Potassium peroxomonosulphate, Phase-transfer catalyst.

INTRODUCTION

Phase-transfer catalysis (PTC) has been a fascinating area of current research interest to the chemists all over the world. It was a novel and versatile technique applicable not only in organic chemistry[1-3] but also in polymer chemistry[4]. Phase-transfer catalyzed free radical polymerization of vinyl monomers with water-soluble initiators such as peroxomonosulphate (PMS), peroxodisulphate (PDS) offer more advantages over the organic soluble initiators like benzyl peroxide (BPO) azobisisobutyronitrile (AIBN). It was found that such water-soluble initiators could be used effectively for bulk or solution polymerization with phase-transfer catalysts such as quaternary ammonium salts $[Q^+X^-]$ and macrocyclic polyethers (Crown ethers)[5-10].

In the presence of phase-transfer catalyst (PTC), the monomer in the organic phase reacted with the initiator in the aqueous phase. The reaction

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was achieved by means of PTC which complexes and solubilizes the water-soluble initiator in the organic phase. Rasmussen and Smith[11] showed that the polymerization with PTC could be conducted at low temperature with high reaction rates for some monomer systems. Balakrishnan and Muniraj[12] reported the kinetics of polymerization *ortho*-, *meta*- and *para*-tolylmethacrylates and $K_2S_2O_8$/tributylbenzylammonium (TBBA) assisted free radical polymerization. They had also reported a kinetic investigation of PTC catalyzed free radical polymerization of acrylonitrile (AN) using $K_2S_2O_8$ as water-soluble initiator in presence of tetramethyl ammonium bromide (TMAB), tetraethyl ammonium bromide (TEAB) and tetrabutyl ammonium bromide (TBAB) as phase-transfer catalysts[13]. They also reported the kinetics of free radical polymerization of acrylonitrile using potassium peroxomonosulphate (PMS) couple with tetrabutyl phosphonium chloride catalyst system[14].

The present article describes the systematic study of kinetics of polymerization of methylacrylate (MA) using potassium peroxomonosulphate/ phase-transfer catalyst (tetrabutyl phosphonium chloride) in ethyl acetate-water bi-phase system.

EXPERIMENTAL

Potassium peroxomonosulphate was obtained from Dupont-De Nemours[15] and used as received (trade name oxone). The phase-transfer catalyst, *viz.*, tetrabutyl phosphonium chloride (Fluka, Buchs, Switzerland) methylacrylate (E. Merck), $KHSO_4$, acetic acid and sodium acetate, ethyl acetate and methanol of analR grade were used. Polymerization experiments were carried out in Pyrex glass polymerization tube in a nitrogen atmosphere at 50 ± 0.1°C without stirring. The reaction mixture consisted of 10 mL aqueous phase and 10 mL of organic phase (ethyl acetate). The reaction mixture was deaerated for 45 min when PMS was added to the reaction mixture, polymerization occurred and polymethyacrylate precipitated continuously during polymerization. At the end of the predetermined reaction time, the polymerization was arrested by pouring the reaction mixture into ice-cold methanol (containing traces of hydroquinone). The polymer yield was determined gravimetrically. The rate of polymerization (Rp) was calculated from the weight of polymer formed using eqn. 1.

$$Rp = \frac{(1000 \times W)}{vtM} \tag{1}$$

where W is weight of the polymer (g), v = volume of the reaction mixture, t = reaction time (s) and M = molecular weight of the monomer.

The viscosities of the polymer samples were determined using Ubbelhode viscometer. The solvent benzene (E. Merck) was taken for measuring the viscosity of samples of polymethylacrylate. The intrinsic viscosity was determined experimentally using the extrapolation method of Kraemer. The molecular weights were calculated using the appropriate Mark-Houwink relationship[16].

$$[\eta] = KM_v^a \tag{2}$$

where K and a are constants for the polymer and solvent used at a specified temperature. From the molecular weights of the polymer, the degree of polymerization $\overline{X}_n$ values were calculated using the relationship

$$\overline{M}_v = \overline{M}_0 \cdot \overline{X}_n (\text{assuming } \overline{M}_n = \overline{M}_v)$$

where $\overline{M}_0$ is the molecular weight of the monomer, $\overline{M}_n$ is the number of average molecular weight, $\overline{M}_v$ is the viscosity of average molecular weight, and $\overline{X}_n$ is degree of polymerization.

RESULTS AND DISCUSSION

Polymerization reactions have been carried out at 50 ± 0.1°C in ethyl acetate and the induction period is found to be negligible. The steady state rate of polymerization was attained after 1.5 h for methylacrylate (Fig. 1). The reaction time was fixed at 90 min to carry out the experiments with variations in other parameters. All the polymerization reactions were carried out at 50 ± 0.1°C up to the conversion of less than 15 %.

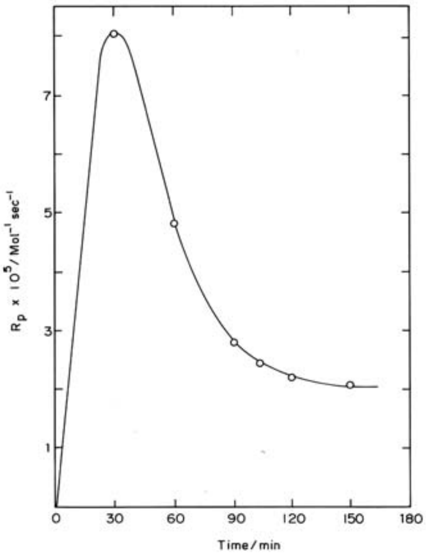

Fig. 1. Steady state of polymerization. Line $R_p \times 10^5$ mol dm^{-3} s^{-3}, [monomer]: 2.0 mol dm^{-3}; [PMS]: 0.02 mol dm^{-3}; [TBPC]: 0.02 mol dm^{-3}, m: 0.05 mol dm^{-3} temp: 50 ± 1°C

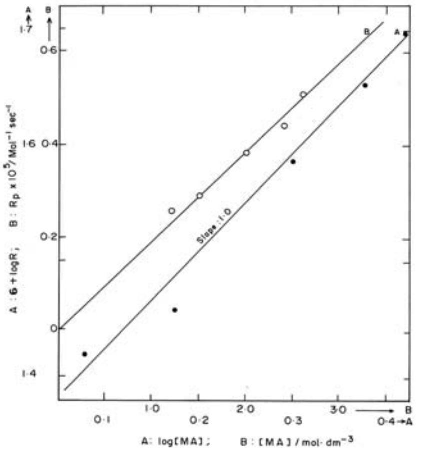

Fig. 2. Effect of [monomer] on R_p Line A: 5 + log R_p *vs.* log [MA]. Line B: $R_p \times 10^5$ mol dm^{-3} *vs.* [MA], [PMS]: 0.02 mol dm^{-3}, [TBPC]: 0.02 mol dm^{-3}, m: 0.05 mol dm^{-3}, temp: 50 ±1°C

Rate of polymerization (Rp) and the effect of [monomer]: Effect of monomer concentration on the rate of polymerization was studied by varying the monomer concentration range [MA]: 0.6-3.8 mol dm^{-3} at fixed concentration of potassium peroxomonosulphate:[PMS] 0.02 mol dm^{-3}, phase transfer catalyst tetrabutyl phosphonium chloride (TBPC): 0.02 mol dm^{-3}. A plot of log Rp *vs.* log [methylacrylate] was found to be linear (Fig. 2) with slope equal to unity clearly indicating the dependence of Rp on [Methylacrylate] and a plot of Rp on [Methylacrylate]$^{1.0}$ were found to be linear passing through origin. A similar order in monomer was reported by Jayakrishnan and Shah[8] in phase-transfer catalyzed polymerization of MMA using ammonium peroxydisulphate/hexadecyl pyridinium chloride in ethyl acetate-water system. Ghosh *et al.*[17] reported the first order dependence of [monomer] in tetrabutyl ammonium bromide assisted free radical polymerization of styrene initiated by potassium peroxomonosulphate at 60°C. A similar order on monomer concentration was observed by Muniraj[19] in the phenyl methylacrylate polymerization initiated by $K_2S_2O_8$/tributyl benzyl ammonium chloride.

Effect of initiator [PMS] on Rp: At fixed [MA]: 2.0 mol dm^{-3} and constant ionic strength 0.05 mol dm^{-3}, the effect of [PMS] on Rp was studied by varying the concentration range from 0.004 to 0.028 mol dm^{-3}. A plot of Rp *vs.* log [PMS] was found to be linear with a slope equal to 0.7 on [PMS] (Fig. 3). A plot of Rp *vs.* [PMS]$^{0.7}$ was found to be linear passing through the origin supporting the above order dependence on [PMS]. A similar initiator order was observed in the polymerization of tributylbenzyl ammonium chloride catalyst system[12]. The order with respect to initiator (0.06) was reported by Rasmussen and Smith[11]. The higher initiator order can be explained by a gel effect[18,19] or diffusion controlled termination rate constant[12,13] whenever termination is bimolecular in the free radical polymerization process, it suggests that the monomer-induced decomposition of PMS was absent.

Effect of phase-transfer catalyst of Rp: At fixed concentration of monomer methylacrylate (MA: 2.0 mol dm^{-3}), potassium peroxomonosulphate (PMS, 0.02 mol dm^{-3}) and constant ionic strength (0.05 mol dm^{-3}), the effect of [TBPC] on Rp was studied by varying [TBPC] in the range 0.006-0.024 mol dm^{-3}. A plot of log Rp *vs.* log [TBPC] was found to be linear with a slope equal to 0.5 inferring that half order dependence on [TBPC] (Fig. 4). A plot of Rp *vs.* [TBPC]$^{0.5}$ was found to be linear passing through the origin supporting the half order dependence on TBPC concentration. A similar order was observed by Jayakrishnan and Shah[8]. The rate of polymerization was found to be proportional to the square root of phase-transfer catalyst concentration in the polymerization of *ortho*-, *meta*- and *para*-tolyl methacrylate initiation by $K_2S_2O_8$/TBBA, $K_2S_2O_8$/TMAB and

$K_2S_2O_8$/TEBA systems[13]. They have also reported the phase-transfer catalyst exponent to be 0.5 in the polymerization of AN with potassium peroxomonosulphate-tetrabutylphosphonium chloride catalyst system[14].

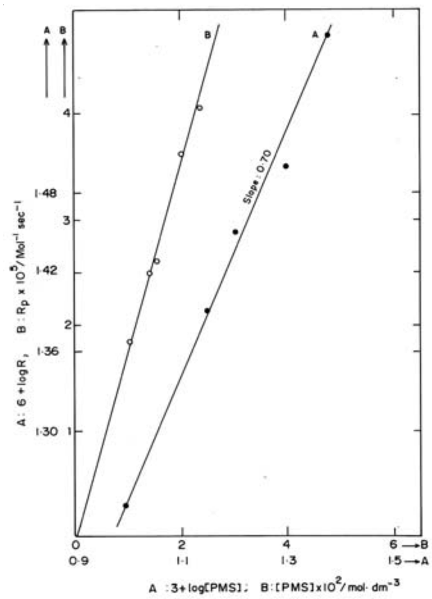

Fig. 3. Effect of [PMS] on R_p Line A: 5 + log R_p *vs.* log [PMS]. Line B: $R_p \times 10^5$ mol dm^{-3} s^{-1} *vs.* [PMS], [Monomer]: 2.0 mol dm^{-3}. [TBPC]: 0.02 mol dm^{-3}, m:0.05 mol dm^{-3}, temp: 50±1°C

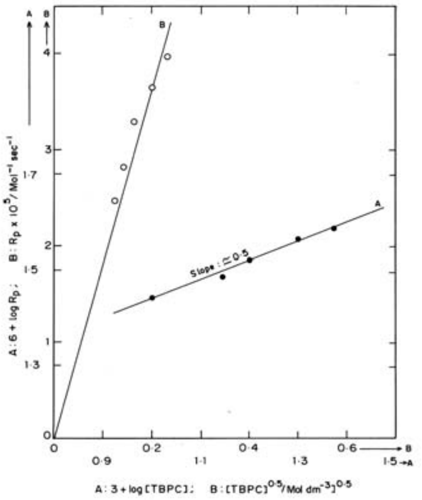

Fig. 4. Effect of [TBPC] on R_p Line A: 5 + log R_p *vs.* log [TBPC]. Line B: $R_p \times 10^5$ mol dm^{-3} s^{-1} *vs.* [TBPC], [Monomer]: 2.0 mol dm^{-3}, [PMS]: 0.02 mol dm^{-3}, m: 0.05 mol dm^{-3}, temp:50 ± 1°C

Effect of ionic strength on Rp: The effect of ionic strength was observed in the range of 0.03-0.07 mol dm^{-3} [$KHSO_4$] at a fixed [MA]: 2.0 mol dm^{-3} and tetrabutyl phosphonium chloride [TBPC]: 0.002 mol dm^{-3}. The variation in ionic strength was found to exert no significant change in the Rp in the present investigation.

Effect of temperature on Rp: Increasing the temperature from 45 to 55°C, the percentage conversion and Rp increased steadily and reached a steady state of 90 min. The activation energy was calculated from the Arrhenius plot of log Rp *vs.* 1/T in the above temperature range. From the Arrhenius plot, the thermodynamic parameters were calculated to be $\Delta H^{\neq} = 69.8$ kJ mol^{-1}, $\Delta S^{\neq} = 123.3$ JK^{-1} mol^{-1} and $\Delta G^{\neq} = 109.8$ kJ mol^{-1}.

Mechanism and rate law: Peroxomonosulphate exists as HSO_5^- in an aqueous solution in the absence of high acidity and alkalinity[20]. First pK_a of PMS is in the high acidity region and second pKa is equal to 9.4 unlike symmetrical peroxide. $S_2O_8^{2-}$ which gives raise to two sulphate radicals on hemolytic scission as shown in eqn. 3 and PMS by a similar process, generates $SO^{\bullet-}$ and $OH^{\bullet-}$ radicals as eqn. 4

$$SO_3-O-O-SO_3^{2-} \rightarrow 2SO_4^{\bullet-} \tag{3}$$

$$HO-OSO_3^{-} \rightarrow OH^{\bullet-} + SO_4^{\bullet-} \tag{4}$$

Phase-transfer

$$Q^{+}_{(w)} + HSO^{-}_{5(w)} \underset{}{\overset{K}{\rightleftharpoons}} [Q^{+}HSO_5^{-}]_o \tag{5}$$

Decomposition

$$2[Q^{+}HSO_5^{-}]_{(o)} + e^{-}_{solvent} \xrightarrow{kd} \begin{cases} Q^{+}SO_4^{\bullet-} + OH^{\bullet-} & (6) \\ OH^{\bullet} + Q^{+}SO_4^{2-} & (7) \end{cases}$$

Initiation

$$R^{\bullet} + M \xrightarrow{k_i} R-M_1^{\bullet} \tag{8}$$

where $R^{\bullet} = OH^{\bullet}$ (or) $Q^{+}SO_4^{\bullet-}$

Propagation

$$R-M_1^{\bullet} + M \xrightarrow{k_p} R-M_2^{\bullet} \tag{9}$$

$$R-M_{n-1}^{\bullet} + R-M \xrightarrow{k_p} R-M_n^{\bullet} \tag{10}$$

Termination

$$R-M_n^{\bullet} + R-M_n^{\bullet} \xrightarrow{k_t} \text{polymer} \tag{11}$$

Applying the general principles of free radical polymerization and steady state hypothesis to the radical species, the rate equation to the present kinetic data can be derived considering the above reaction steps (5-11).

Rate of initiation Ri = Ri$[R^{\bullet}]$[M]

$$-d[R^{\bullet}]/dt = 2kd[Q^{+}HSO_5^{-}]_{(o)}/ki[R^{\bullet}][M] \tag{12}$$

$$[R^{\bullet}] = 2kd[Q^{+}HSO_5^{-}]_{(o)}/ki[M] \tag{13}$$

Substituting the values of $[Q^{+}SO_5^{-}]_{(o)}$ from eqn. 5 into 13 and substituting $[R^{\bullet}]$ in eqn. 12 becomes

$$R_i = 2kd\,k[Q^{+}]_{(w)}[HSO_5^{-}]_{(w)} \tag{14}$$

Rate of termination

$$R_t = 2kt[R-M_n^{\bullet}]^2 \tag{15}$$

At steady state, the rate of initiation is equal to the rate of termination in the free radical polymerization

$R_i = R_t$

$$2\text{kd k}[\text{Q}^{+}]_{(\text{w})}[\text{HSO}_5^{-}]_{(\text{w})} = 2\text{kt}[\text{R}-\text{M}_n^{\bullet}]^2$$

$$[\text{R}-\text{M}_{n\bullet}] = \text{k}(\text{kd}/\text{kt})[\text{Q}^{+}]_{(\text{w})}^{0.5}[\text{HSO}_5^{-}]_{(\text{w})}^{0.5} \tag{16}$$

The rate of polymerization is

$$-\text{d}[\text{M}]/\text{dt} = \text{k}_\text{p}[\text{M}][\text{R}-\text{M}_n^{\bullet}] \tag{17}$$

Substituting the above value $[\text{R}-\text{M}_n^{\bullet}]$ from eqn. 16 in eqn. 17,

$$-\text{d}[\text{M}]/\text{dt} = \text{R}_\text{p} = \text{k}_\text{p}[\text{Kk}_\text{d}/\text{k}_\text{t}]^{0.5}[[\text{Q}^{+}]_{(\text{w})}^{0.5}[\text{HSO}_5^{-}]_{(\text{w})}^{0.5}[\text{M}]_{(\text{o})}^{1.0} \tag{18}$$

The derived rate equation (18) agrees well with the experimental results observed. The kinetic results are supplemented with viscosity studies. The degree of polymerization $(\overline{\text{X}}_\text{n})$ was evaluated from the intrinsic viscosity data of the polymer solution. The expression for the degree of the polymerization is given by the ratio of rate of propagation to rate of termination.

$$\overline{\text{X}}_\text{n} = \frac{\text{R}_\text{p}}{\text{R}_\text{t}} = \frac{\text{K}_\text{p}[\text{M}]^{1.0}}{[2[\text{k}_\text{d}\text{K}/\text{k}_\text{t}]^{0.5}[\text{Q}^{+}]_{(\text{w})}^{0.5}[\text{HSO}_5^{-}]_{(\text{w})}^{0.5}} \tag{19}$$

Eqn. 19 requires that the degree of polymerization should be proportional to $[\text{M}]^{1.0}$ and inversely proportional $[\text{initiator}]^{0.5}$. It was found that a plot of $\overline{\text{X}}_\text{n}$ *vs.* $[\text{monomer}]^{1.0}$ was linear with zero intercept (Fig. 5). This observation supports the proposed mechanism.

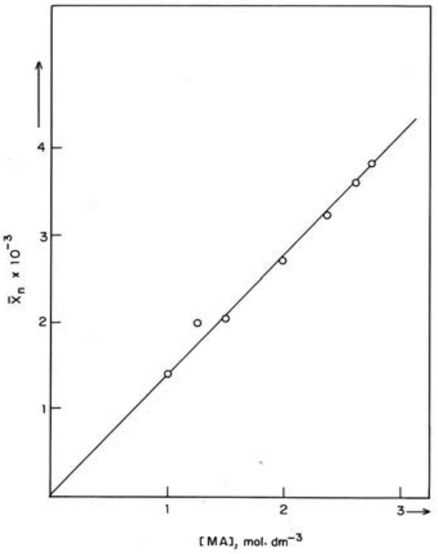

Fig. 5. Effect of monomer on degree of polymerization
Line $\overline{\text{X}}_\text{n} \times 10^{-3}$ *vs.* [MA] mol dm^{-3}

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