KINETICS AND MECHANISM OF PHASE TRANSFER CATALYZED FREE RADICAL POLYMERIZATION OF METHYL ACRYLATE

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ABSTRACT

The kinetics of free radical polymerization of methylacrylate (MA) was investigated using benzyltributylammonium chloride (BTBAC) as phase transfer catalyst and potassium peroxydisulfate as initiator at aconstant temperature, 60°C, in an inert atmosphere under unstirred condition. The effect of concentrations of the monomer, initiator and the catalyst on polymerization was discussed and a mechanism of polymerization has been proposed. The order with respect to the monomer, initiator, and phase transfer catalyst was found to be 2, 0.5, and 0.5, respectively.

INTRODUCTION

Phase transfer catalysis is a technique which enabled the chemists to carry out a reaction between two immiscible reactants. In this method, the phase transfer catalyst (PTC), forms a complex with the initiator and carries it from

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aqueous phase to organic phase to initiate the reaction where the substrate is present. A wide variety of reactions such as alkylation, acylation, oxidation, reduction, elimination, hydrolysis etc., have been studied using phase transfer cataylst [1]. Polymers prepared by this method include polycarbonates [2], polysulfonates [3], polyphosphonates [4], polyethers [5], polyesters [6], etc. The var-ious commonly used catalysts are quarternary ammonium salts, crown ethers, cryptands and polyethyleneglycols.

The first report on the phase transfer catalyst assisted free radical polymerization was by Rasmussen and Smith [7, 8]. They reported the polymerization of butyl acrylate with different crown ethers as phase transfer catalysts and potassium peroxydisulfate as water soluble initiator. Jayakrishnan and Shah [9, 10] studied the polymerization of acrylonitrile and methyl methacrylate using hexadecylpyridinium chloride as PTC, in ethyl acetate-water medium. Mandal and Gosh [11] investigated the free radical polymerization of styrene and methyl methacrylate using tetrabutylammonium bromide as phase transfer catalyst and potassium peroxydisulfate as initiator. Umapathy and Balakrishnan [12] studied the kinetics of free radical polymerization of methyl methacrylate with ammonium peroxydisulfate-benzyltributylammonium chloride (BTBAC) system.

However, the kinetics of the phase transfer catalyzed polymerization of methyl acrylate using peroxydisulfate as initiator has not been studied so far. This prompted us to investigate a detailed kinetic study on the polymerization of methyl acrylate using, BTBAC as phase transfer catalyst and potassium peroxydisulfate as water soluble initiator in ethyl acetate-water biphase medium.

EXPERIMENTAL

Methyl acrylate (MA), potassium peroxydisulfate, methanol, acetone, ethyl acetate were purified by a standard procedure. BTBAC was used as received, and the water used was laboratory distilled. Polymerization was carried out in a Pyrex glass tube in an inert atmosphere under unstirred conditions. The reaction mixture comprised 10 ml of organic phase containing monomer and solvent (ethyl acetate) and 10 ml of aqueous phase containing potassium peroxydisulfate, BTBAC, and sulphuric acid and potassium bisulfate were used to maintain acid and ionic strength, respectively. When potassium peroxydisulfate was added to the reaction mixture, polymerization started, and a precipitate formed continuously during polymerization. The reaction was arrested by pouring the reaction mixture into ice-cold methanol containing traces of hydroquinone [13]. The rate of polymerization was determined gravimetrically [12].

RESULTS AND DISCUSSION

The steady state rate of polymerization was first arrived at by determining R_p at different time intervals, and it was found to be 90 minutes (Figure 1). The reaction time was fixed at 90 minutes to carry out the experiments with variation in other parameters.

Effect of Monomer Concentration on the Rate of Polymerization (R_p)

The effect of methylacrylate concentration on the R_p was studied by varying methylacrylate concentration from 2.3 to 3.3 M at fixed concentration of initiator, phase transfer catalyst, acid, and ionic strength. The rate of polymerization increases with an increasing monomer concentration (Figure 2). The order with respect to monomer is deduced from a plot of log R_p versus log [MA] which is linear and the order is found to be 2. Furthermore, a plot of R_p versus $[MA]^2$ was found to be linear passing through the origin confirming the above observation. A reaction order greater than unity with respect to monomer concentration is not uncommon in polymerization reaction. There are many reports on polymerization where R_p shows a higher order than first order dependence on [M] [14, 15, and 16]. The higher order may be caused by a dependence of initiation rate on the monomer concentration. Such a situation could occur when [M] is low or when $k_d > k_i$. Due to the decrease in the mobility of the primary radicals, the initiation sequence becomes the rate determining step.

The second order dependence on R_p on the [M] occurs when termination is by bimolecular reaction of the propagation radicals. The derivation from the
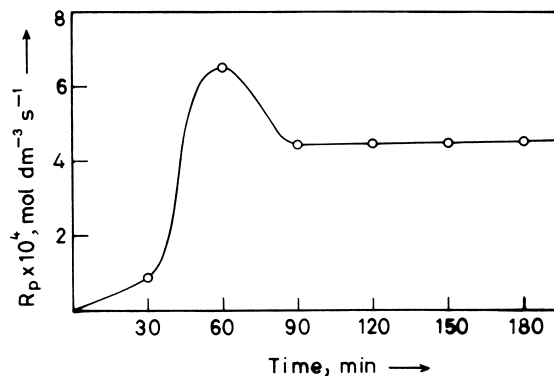
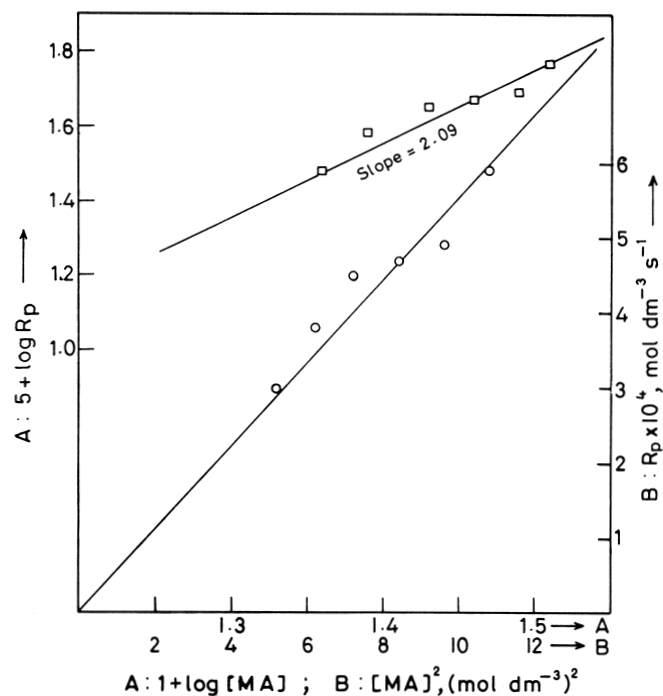**Figure 1.**   Steady state approximation.

Figure 2.   Effect of [monomer] on R_p.

first order dependence may also be due to occlusion phenomenon occurring during polymerization. However, at temperatures of about 60°C, the occurrence of occlusion is negligible [16] and hence occlusion cannot be accounted for in this case in altering the normal kinetic features. Hence, the higher monomer order in the present study can be attributed to the dependence of initiator rate on [M]. Further, the monomer order may be significantly influenced by the variation in diffusion controlled termination rate constant. Either or both of these factors could have contributed to the higher reaction order of two with respect to monomer concentration of methyl acrylate.

Effect of Initiator Concentration on Rate of Polymerization (R_p)

The effect of initiator concentration on R_p was studied by carrying out the reaction at various initiator concentrations in the range 0.025 to 0.040 M at a fixed concentration of monomer, phase transfer catalyst, acid strength and ionic strength. R_p was found to increase with an increasing concentration of the initiator. The plot of log R_p versus log [$K_2 S_2 O_8$] is linear with a slope of 0.5 indicating half order dependence on R_p with respect to [$K_2 S_2 O_8$]. A plot of R_p versus
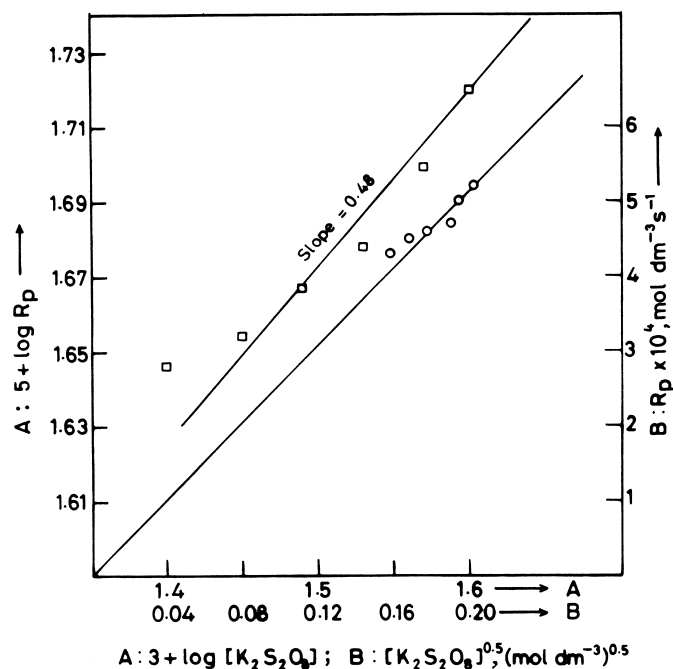
Figure 3. Effect of [initiator] on R_p.

$[K_2 S_2 O_8]^{0.5}$ is linear passing through the origin confirming the above observation (Figure 3). The order with respect to initiator is observed to be 0.5 wherever termination is bimolecular in the free radical polymerization process.

Effect of Phase Transfer Catalyst Concentration on the Rate of Polymerization (R_p).

The effect of concentration of phase transfer catalyst, 0.025 to 0.040 M on the rate of polymerization was studied at definite concentration of monomer, initiator, acid strength and ionic strength. The order with respect to the concentration of the catalyst is found to be 0.5 from a plot of log R_p versus [PTC]. A plot of R_p versus [PTC]$^{0.5}$ is linear passing through the origin confirming the above result (Figure 4).

Effect of Solvent on the Rate of Polymerization (R_p)

The effect of solvent on R_p, was examined by carrying out the polymerization in three different solvents viz., cyclohexane, ethyl acetate, and cyclohexanone having the dielectric constant 2.02, 6.02, and 18.3, respectively. It was found that the rate of polymerization decreased in the following order:
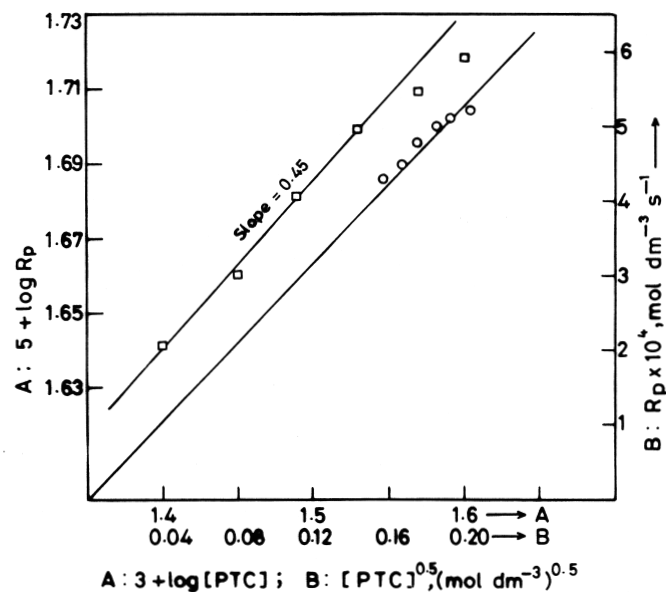
Figure 4. Effect of [PTC] on R_p.

Cyclohexanone > Ethyl acetate > Cyclohexane

Since the quarternary ammonium peroxydisulfate $(Q^+)_2 S_2 O_8^{2-}$ is an ionic species, it may be transferred to the organic medium to a greater extent with the increasing dielectric constant of the medium. In addition, the increase in dielectric constant of the medium would favor separation of ions and enhance the rate of propagation and retard the rate of termination. Hence, there will be an increase in the rate of polymerization with an increase in dielectric constant of the organic medium [17, 18].

Effect of Temperature on the Rate of Polymerization (R_p)

The effect of temperature was studied at different temperatures in the range 50 to 65°C at a fixed concentration of monomer, initiator, catalyst, acid strength, and ionic strength. R_p is found to increase with an increase in temperature (Figure 5). From a plot of log R_p versus 1/T, the activation energy (E_a) was calculated and is found to be 17.79 k cal.mol^{-1}.
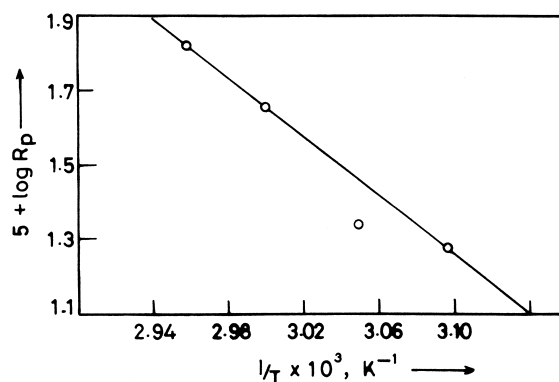
Figure 5.   Effect of temperature on R_p.

Effect of Acid and Ionic Strength on Rate of Polymerization (R_p)

A variation in acid and ionic strength had no significant change in the rate of polymerization.
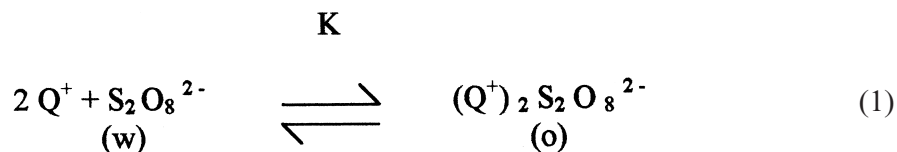
Mechanism and Rate Law

To explain the experimental observations, a mechanism has been proposed. The two factors which involve in phase transfer catalyzed polymerization are:

(1) The phase transfer catalyst forms quaternary ammonium peroxydisulfate ion pair $(Q^+)_2\,S_2\,O_8^{2-}$ in the aqueous phase and migrates to the organic phase containing the monomer.

(2) The ion-pair $(Q^+)_2\,S_2\,O_8^{2-}$ migrated to the organic phase undergoes decomposition producing $Q^+\,SO_4^{-}$ which initiates polymerization of the monomer in the organic phase.

Phase transfer

$$2\,Q^+ + S_2O_8^{2-} \underset{}{\overset{K}{\rightleftharpoons}} (Q^+)_2\,S_2\,O_8^{2-} \qquad (1)$$
$$\text{(w)} \qquad\qquad\qquad\qquad \text{(o)}$$

Initiation

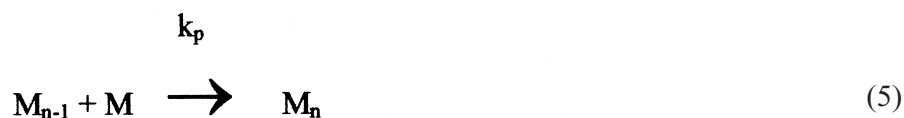$$(Q^+)_2 S_2 O_8{}^{2-} \xrightarrow{k_d} 2 Q^+ SO_4{}^- \qquad (2)$$
$$\text{(o)} \qquad\qquad \text{(o)}$$

$$Q^+ SO_4{}^- + M \xrightarrow{k_i} M_1 \qquad (3)$$

Propagation

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

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

Termination

$$2M_n \xrightarrow{k_t} \text{Polymer} \qquad (6)$$
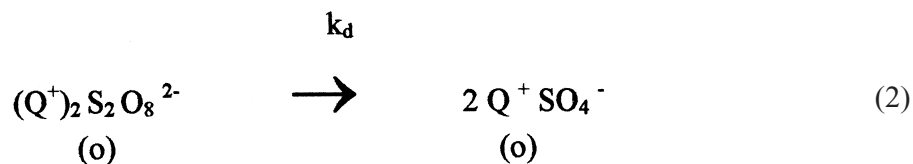
The subscripts (w) and (o) refers to aqueous and organic phase, respectively. Applying the general principles of free radical polymerization and stattionary state hypothesis to the radical species, the rate law for this mechanism has be derived as

$$R_p = k_p \frac{(k_d K)^{0.5}}{(k_t)^{0.5}} \cdot \frac{[M]^2 [S_2 O_8{}^{2-}]_w{}^{0.5} [Q^+]_{Total}}{(1 + K [Q^+]_w [S_2 O_8{}^{2-}]_w)} \qquad (7)$$

where $[Q^+] = [Q^2]_w + [(Q^+)_2\ S_2\ O_8^{\ 2-}]_o$. This equation satisfactorily explains the above observations.

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