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Competency of sonolysis on PTC induced polymerization of EMA – A comparative kinetic study

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In the presence of biphasic medium, ethyl methacrylate has been polymerized using phase transfer catalyst under silent/ultrasonic condition (53 KHz, 100 W) at 60°C (±1°C) as well as under inert atmosphere. A series of quaternary ammonium salts namely 1,4-Bis(dimethylhexyl)ethylenediammonium bromide (DMHEDAB), 1,4-Bis(dimethylheptyl) ethylenediammonium bromide (DMH1EDAB) and 1,4-Bis(dimethyloctyl) ethylenediammonium bromide (DMOEDAB) have been selected as phase transfer catalysts (PTCs). Rate of polymerization is assessed in silent and sonolytic conditions by varying the concentrations of monomer, initiator, PTCs, solvents, and temperature. The synergism of sonolysis and phase transfer catalysts increased the rate when compared to silent polymerization. Based on the results, thermodynamic values are measured, and the order of efficacy of all three catalysts are observed as DMOEDAB > DMH1EDAB > DMHEDAB.

Keywords: Kinetics, Phase-transfer catalysis, Polymerization, Reaction mechanisms, Sonolysis

Introduction

Radical polymerization techniques are predominantly used to produce polymers with a high molecular weight due to its widespread availability and utility by both industrialists and academics[1-5]. Chemical reactions that are inaccessible due to reactant immiscibility are overcome by phase transfer catalysts (PTC)[6]. The reactants present in different phases namely aqueous and organic are made available to react with each other by catalytic amount of phase transfer reagents thereby increasing the yields, rate of the reaction, etc. The reactive anions existing in the aqueous phase are extracted by the PTC and transported to organic phase where the reactants reside. The solubility problems of ionic and nonpolar compounds are overcome by employing the PTC. Quaternary ammonium and phosponium salts, cryptands, crown ethers, and polyethylene glycols are commonly used in phase transfer catalysis[7-9]. Among them quaternary salts are generally preferred because of their availability, reasonable price, etc.

The incorporation of water based initiators such as potassium and ammonium peroxydisulphate (PDS and ADS, respectively) in phase transfer catalysed polymerization of alkyl monomers is a novel research topic. Multisite PTCs are gaining more attraction than single site because of the involvement of more active sites and intensification of catalytic activity. Recently non-conventional, eco-friendly procedures like microwave, ultrasound irradiation[10-14] has emerged and found extensive application in the modern industrial world. The ultrasonication method is now recognised as an environmentally friendly alternative to traditional methods[15]. Ultrasound has several advantages, including increased yield, faster reaction time[16], and energy efficiency. The use of ultrasound in liquid-liquid phase transfer catalysis has received a great deal of attention lately[17]. The popularity of ultrasound irradiation in organic synthesis has grown significantly in recent years.

The primary aim of using PTC in combination with ultrasonication is to create a more favourable environment and speed up reaction time[18-23]. Due to the formation of fine emulsions by ultrasound, the interfacial contact area is increased, which favourably affects the outcome[24]. It was reported that reaction rate is enhanced by employing sonolysis on liquid-liquid PTC[25]. A notable increase in reaction rate was observed in the Cannizzaro reaction[26], which was catalysed by PTC under sonolytic conditions. The impact of ultrasonic irradiation on the synthesis of polymers was reported[27]. The unusual reactivity caused by ultrasonic irradiation is sure to find significant industrial applications[28]. The literature sparked curiosity in comparing the rate of polymerization by combining phase transfer catalysis and ultrasound.

As a result, polymerization of ethyl methacrylate was carried out under silent and sonolytic conditions with homologous quaternary ammonium salt series, specifically 1,4-bis(dimethylhexyl)ethylenediammonium bromide (DMHEDAB), 1,4-bis (dimethylheptyl) ethylenediammonium bromide (DMH1EDAB) and 1,4-bis(dimethyloctyl)ethylenediammonium bromide (DMOEDAB) were used as phase transfer catalysts.

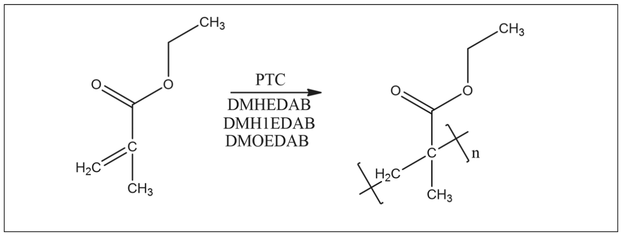
Experimental Section

Materials and method

Ethyl methacrylate with 0.92 g/cm^3 density and 99% purity and potassium peroxydisulphate (97%) were obtained from (Loba Chemie, Chennai, India). SRL Chemicals, India, supplied cyclohexanone (99%) and methanol (99%). The reactions were carried out with double-distilled water. An ultrasonicator with a frequency of 53 kHz; an output of 100 W and a holding capacity of 3.0 L water was used for this study.

Polymerization under silent and sonolytic conditions

The polymerization reaction (Scheme 1) was performed in an inert atmospheric condition and at the temperature of 60°C (±1°C) with/without ultrasonic condition (53 kHz, 100 W). A pyrex polymer tube and a nitrogen atmosphere were used to conduct the reaction. The organic phase containing 4.0 mol L^{-1} of EMA in cyclohexanone, and the aqueous phase containing identified PTC of strength 2.0x 10^{-2} mol L^{-1}, as well as potassium peroxydisulphate and sulphuric acid to retain ionic and acid strength were taken. For 40 min, the polymeric tube containing the biphasic mixture was positioned in the ultrasonic bath's centre to receive the most energy. The addition of initiator triggered the reaction (PDS). The micro-turbulence created by ultrasound helped in a uniform initiator concentration. The ultrasound activated the formation of fine dispersions of monomer which in turn induced the rapid polymerization of ethyl methacrylate[29]. The reaction was decelerated by adding the reaction mixture to ice-cold methanol. After being washed with distilled water and methanol, the precipitated polymer was dried in an oven at 50 to 60°C. Similar procedure was adopted for silent polymerization without using ultrasonicator. The rate of polymerization (Rp) (mol L^{-1} s^{-1})[30] was determined by using the following equation.



Scheme 1 — Phase transferred catalysed radical polymerization of EMA

$$Rp = 1000 * W/V * t * M \qquad ...(1)$$

Here W denotes weight of the polymer (g), V represents volume of the reaction mixture (mL), t stands for reaction time (s), M denotes molecular weight of the monomer (g/mol).

Results and Discussion

Significance of sonolysis

An analysis of the kinetic effects of ultrasound on the polymerization of EMA was done. A combo of PTC and ultrasound produces enhanced the effect compared to the performance of single technique. PTC starts the reaction across the interface, and ultrasound speeds up the transfer[31-33].

Steady state rate of polymerization

Time was varied while other parameters such as monomer, catalysts, initiator, ionic and acid strength concentrations remained constant to assess the steady state rate of polymerization. The temperature was maintained at 60 ± 1°C. The *Rp* vs. time plot (Fig. 1a and 1b) exhibits an increase to a certain magnitude, followed by a slight decrease, and then it remains constant after that. The rise and decline in *Rp* can be ascertained that, when the medium is less viscous, the reaction rate increased, and as it progressed the rate of polymerization declined due to high viscous state. The time required to achieve constant was found to be 40 min. At the same time, the figures depict that, decrease in *Rp* for silent and increase *Rp* in presence of ultrasonic irradiation. It's possible that ultrasonic irradiation sped up the polymerization

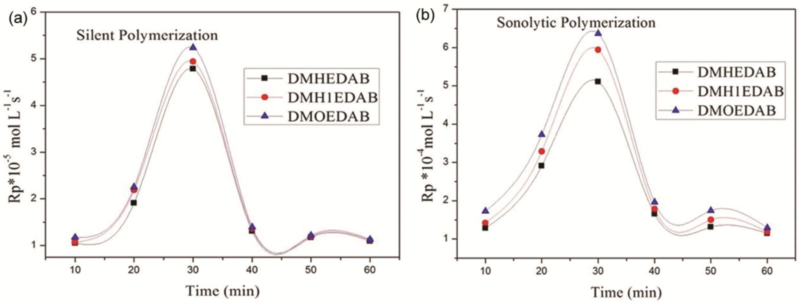


Fig. 1 — (a-b) Steady state approximation. Polymerization condition: [EMA]: 4.0 mol L^{-1}; [PDS]: 2.0 x 10^{-2} mol L^{-1}; [PTC]: 2.0 x 10^{-2} mol L^{-1}; temperature: 60 ± 1°C; ultrasonic condition: 53 kHz, 100 W

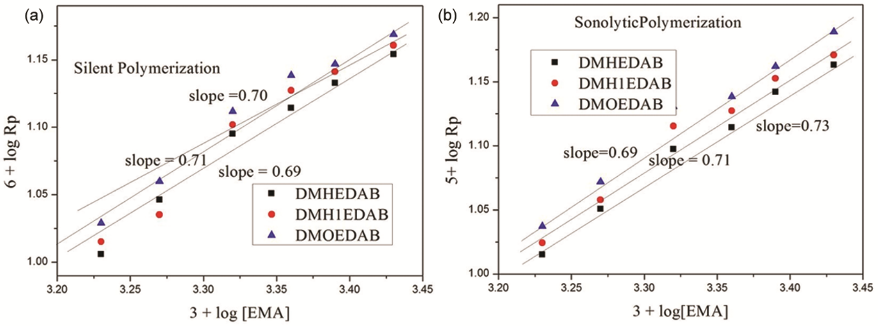


Fig. 2 — (a-b) Role of monomer concentration on Rp

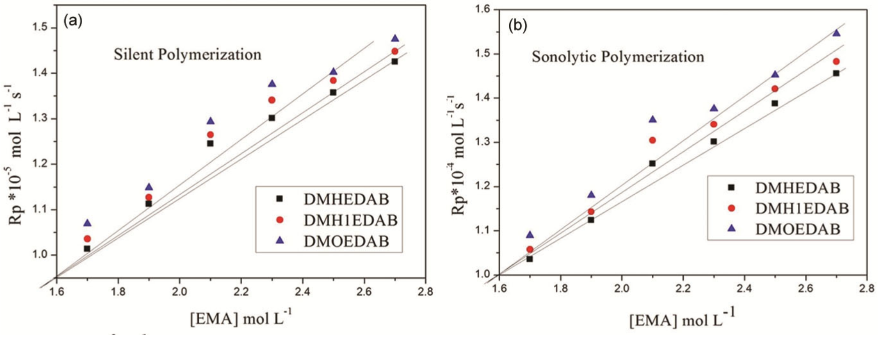


Fig. 3 — (a-b) Derivative plot for monomer

process by vigorously combining the organic and aqueous phases to mimic a homogeneous solution.

Impact of monomer on *Rp*

The reaction rate was assessed by changing the concentration of monomer from 1.7 to 2.7 mol L^{-1} while holding the other variables constant and in both sonolytic and non-sonolytic conditions. As concentration of monomer increased, *Rp* also increased as expected. By increasing the concentration the availability of monomer molecules had been increased for free radicals that is via PTC, hence the *Rp* increased. The reaction order for all three PTCs under silent/sonolytic conditions was 0.69, 0.70, and 0.71, as shown by the plot of log *Rp* vs. log [EMA] in Fig. 2. The plot of *Rp* against [EMA] passes through the origin in Fig. 3, which supports the aforementioned observation. With respect to monomer concentration an order of unity had been established using PTC during the polymerization of various vinyl monomers[34-35,40].

Rp and initiator concentration

In both silent and sonolytic conditions, *Rp* was evaluated maintaining the initiator concentration in the range of 0.16–0.27 mol L^{-1} and other parameters like PTC, pH, and monomer as kept constant. Fig. 4 shows a linear relationship between log *Rp* vs log PDS. Fig. 5 show a plot of *Rp* vs [PDS] that passes through the origin.

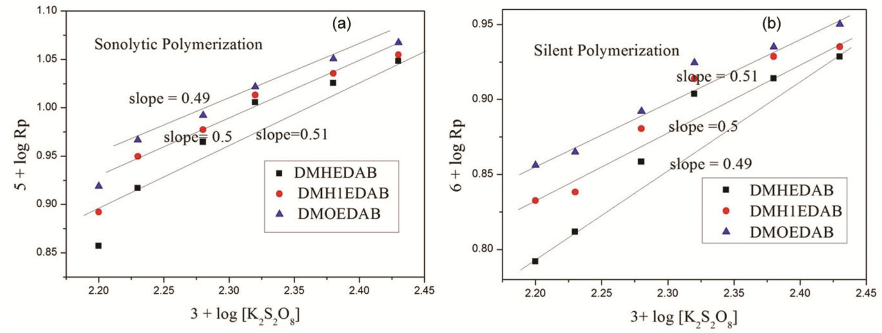


Fig. 4 — (a-b) Role of initiator concentration on Rp

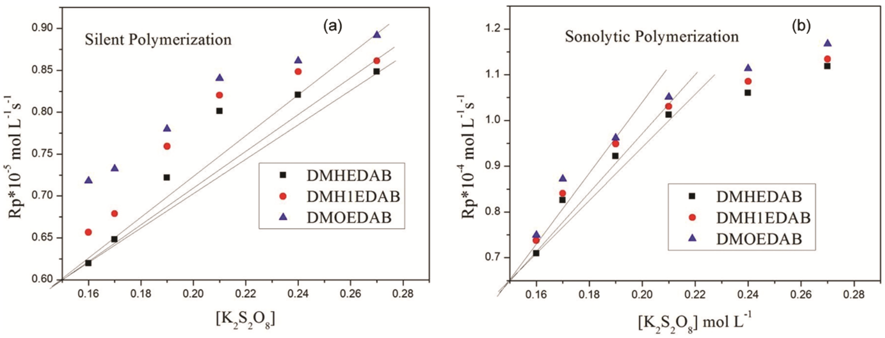


Fig. 5 — (a-b) Derivative plot for initiator

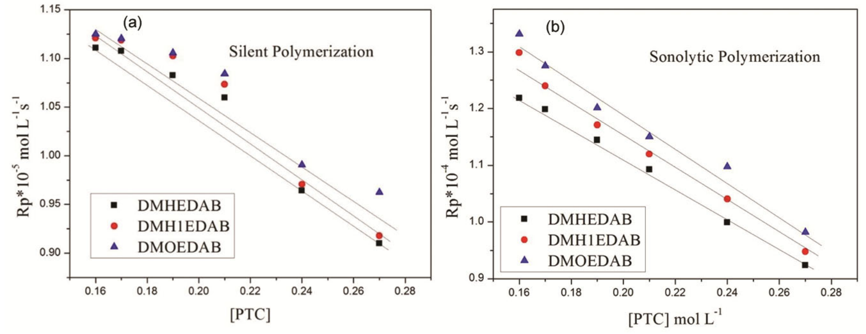


Fig. 6 — (a-b) Role of catalyst concentration on Rp

Higher *Rp* in presence of ultrasound may be due to active formation of highly lipophilic complex between PDS and PTC (QS_2O_8). QS_2O_8 preferentially moves from the aqueous to the organic phases due to its lipophilic nature. This facilitates the monomer and QS_2O_8 to react quickly thus leads to the formation of polymer. The order of the reaction was found to be 0.5(Ref.36). In phase transfer catalyzed polymerization reactions, orders higher than 0.5 with respect to the initiator have been observed[37].

Rp and catalyst concentration

The relationship between *Rp* and PTC concentration was investigated without changing any other parameters except the concentration of PTC was varied in the range of 0.16-0.27 mol L^{-1} with/without ultrasound wave (53 kHz, 100 W). Rate of polymerization was found to be decreased as the catalyst concentration increased as shown in Fig. 6.

As catalyst concentration rose, researchers[38-39] also found a decline in polymerization rate. Ultrasound just facilitates the transfer by expanding the contact area across which it occurs. The function of PTC is to initiate the process by transferring species across the interface. However, for both silent and sonolytic conditions, as the concentration increased, the rate of polymerization decreased. It could be ascribed to the bulky group

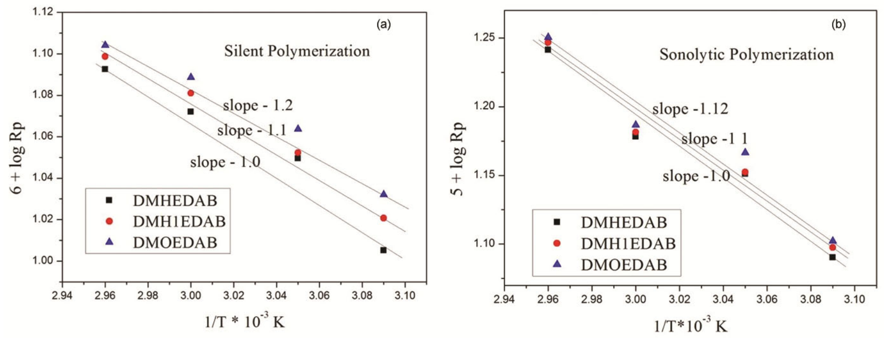


Fig. 7 — (a-b) Role of temperature on Rp

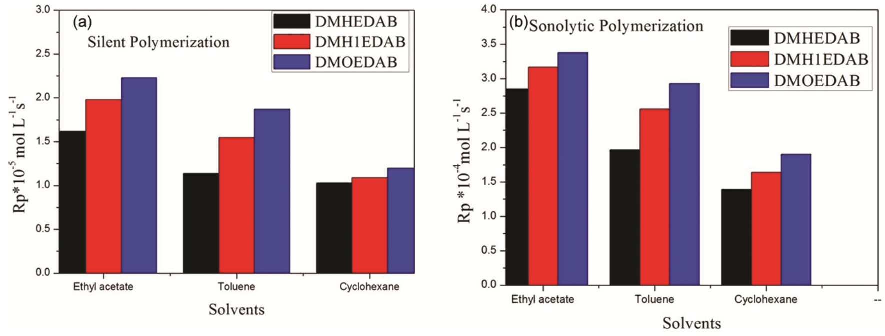


Fig. 8 — (a-b) Role of solvent on Rp

Table 1 — Thermodynamic parameters

PTC	*Ea* (kJ/mol)	*ΔG#* (kcal/mol)	*ΔH#* (kcal/mol)	*ΔS#* (kJ/mol)
DMOEDAB	19.15	75.11	18.49	-171.58
DMH1EDAB	21.44	77.35	20.79	-171.39
DMHEDAB	23.16	78.94	22.51	-171.00

in the catalyst posing a steric hindrance. At higher concentrations, the bulky group might have made it more difficult for anions to transfer effectively to the organic phase. It could also be related to free energies, because halide ions prefer the aqueous phase over the organic phase.

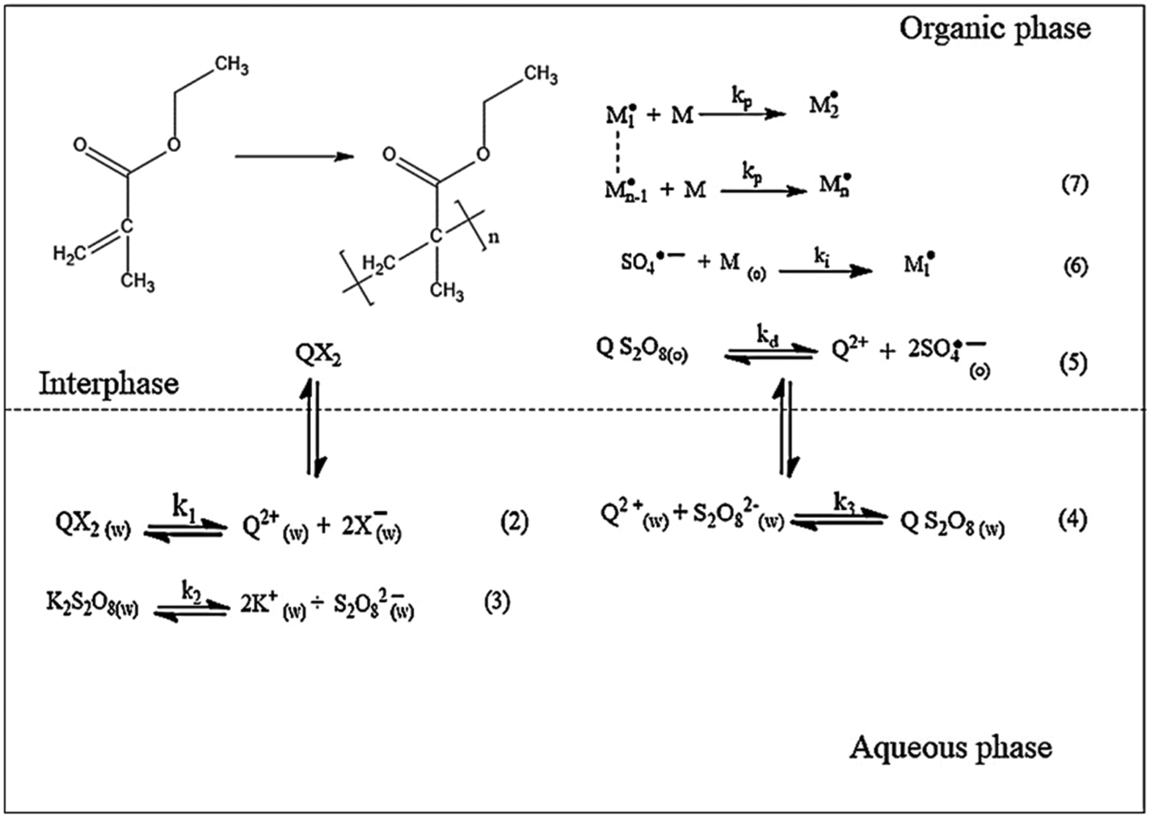
Impact of temperature on Rp

The Rp was determined as a function of temperature spanning a range of 50 to 65°C under both silent and sonolytic conditions. The Rp for both conditions are shown in Fig.7a and 7b with respect to temperature. Sonolytic polymerization exhibited an increase compared to silent conditions.

The major contributing factor for the increased rate in the sonolytic polymerization might be the formation of free radicals at faster rate. When the energy of activation (*Ea*) was determined using the Arrhenius plot, it was found that sonolytic conditions had lower *Ea* values than silent conditions. Other thermodynamic parameters shown in Table 1 include activation enthalpy (H), activation entropy (S), and activation free energy (Ea).

Effect of solvent on *Rp*

Three different solvents: cyclohexane, ethyl acetate, and toluene, with dielectric constants of 2.02, 6.02, and 2.4, respectively, were used to polymerize EMA. The influence of solvent on Rp is depicted in Fig.8a and 8b for both silent and sonolytic conditions. The order in which Rp increased was as follows: ethyl acetate > toluene > cyclohexane. Actually, the rate of polymerization rises as the organic medium's polarity increases, which is a result of the facilitation of PDS transfer to the organic phase. The solvating power of the reaction medium increases as the dielectric constant increases, which indirectly increases the number of free ions and, as a result, the rate of polymerization. Sonolytic polymerization occurred at a faster rate than silent polymerization.



Scheme 2 — Travel path of PTC in EMA-$K_2S_2O_8$ system

Effect of ionic strength (µ) and acid strength [H^+]

Changing the acidity and ionic strength of the medium had no effect on *Rp*.

Mechanisms and rate law

Usually, there are two main processes takes place in phase transfer-catalyzed polymerization reactions. These two processes involved the movement of active species from the aqueous phase to the organic phase and the interaction of the moved species with the monomer of the organic phase.

Paths in polymerization

The term "QX_2" states to the phase transfer catalyst and the terms "k_1," "k_2," and "k_3" denote equilibrium constants of initiation, propagation, and termination. Dissociation constant, initiation, propagation, and termination rates are denoted by the terms k_d, k_i, k_p, and k_t, respectively. This mechanism produces quaternary ammonium peroxodisulphate complex ($Q_2S_2O_8^{2-}$) in the aqueous phase, then moves it to the organic phase where it transforms into $Q^+SO_4^-$. The study state hypothesis and the general free radical polymerization principle were both applied to the radical species in order to determine the rate law for this mechanism (Scheme 2).

The equilibrium constants can be given as

$$k_1 = \frac{[Q^{2+}]_w [X^-]^2{}_w}{[QX_2]_w} \quad ...(8)$$

$$k_2 = \frac{[K^+]^2{}_w [S_2O_8^{2-}]_W}{[K_2S_2O_8]_w} \quad ...(9)$$

$$k_3 = \frac{[QS_2O_8]_w}{[Q^{2+}]_w [S_2O_8^{2-}]_w} \quad ...(10)$$

The rate of initiation, Ri, for the sulphate ion free radical is represented as in Eq. (5).

$$R_i = \frac{d[SO_4^{\bullet-}]_w}{dt} = 2k_d f k_3 [Q^{2+}]_w [S_2O_8^{2-}]_W \quad ...(11)$$

Where f is the efficiency of the initiator;

The propagation rate from Eq. (7) can be expressed as

$$R_p = k_p [M^\bullet][M] \quad ...(12)$$

$$[M^\bullet] = \frac{R_P}{k_p[M]} \quad ...(13)$$

When two propagating chains collide during radical polymerization, the polymer is terminated, and this is symbolized as

$$2M_n^{\bullet} \xrightarrow{k_t} \text{Polymer} \qquad \text{...(14)}$$

The termination rate equation can be expressed as

$$R_t = 2k_t[M^{\bullet}]^2 \qquad \text{...(15)}$$

The rate of initiation is equal to the rate of termination at the steady-state,

i.e. $R_i = R_t$ (16)

Based on Eqs (11) and (15)

$$2k_d f k_3 [Q^{2+}]\ \ _w[S_2O_8^{2-}]_W = 2k_t[M^{\bullet}]^2 \qquad \text{...(17)}$$

$$[M^{\bullet}]^2 = \frac{k_d f k_3 [Q^{2+}]\ \ _w[S_2O_8^{2-}]_W}{k_t} \qquad \text{...(18)}$$

$$[M^{\bullet}] = \left(\frac{k_d f k_3 [Q^{2+}]\ \ _w[S_2O_8^{2-}]_W}{k_t}\right)^{1/2} \qquad \text{...(19)}$$

From Eqs (12) and (19)

$$R_P = k_p \left[\frac{k_d f k_3}{k_t}\right]^{1/2} [Q^{2+}]^{0.5}\left[S_2\, O_8{}^{2-}\right]^{0.5}[M]^1 \qquad \text{...(20)}$$

Conclusion

The current study examined the effectiveness of three different phase transfer catalysts, DMHEDAB, DMH1EDAB, and DMOEDAB, in the free radical polymerization of ethyl methacrylate when exposed to ultrasonic irradiation in a cyclohexanone/water biphase medium and an inert atmosphere. Testing was done both with and without ultrasound irradiation to determine the factors affecting polymerization rate. Rate of polymerization increases with monomer and initiator concentrations but decreases with catalyst concentration. An appropriate mechanism has been assessed based on the kinetic study. The overall rate of the reaction for ultrasonic induced phase transfer catalysed polymerization was found to be greater than that of non-induced phase transfer catalysed polymerization.

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