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Efficiency of single and di- site phase transfer catalyzed polymerization of glycidyl methacrylate in the two-phase system: A kinetic study

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In the present kinetic study, glycidyl methacrylate has been polymerized using synthesized single-site phase transfer catalyst - 2-benzoylethyldecyldimethylammonium bromide and di-site –phase transfer catalyst -1,1,4,4-tetramethyl-1,4 dioctylethylenediammonium bromide along with potassium peroxydisulfate as the initiator in inert medium and at a constant temperature of 60°C. The effect of concentrations of the monomer, initiator, catalyst, ionic strength, *p*H and solvent polarity on the rate of polymerization has been examined. The order with respect to the monomer, initiator, and phase transfer catalyst was found to be 1, 0.5, and 0.5, respectively. A suitable polymerization mechanism is proposed. Ionic strength and *p*H has no impact on the rate of polymerization. It is observed that, as the solvent's polarity increased, the rate of polymerization also increased. Di-site phase transfer catalyst results in a higher rate of polymerization compared with single-site phase transfer catalyst while polymerizing glycidyl methacrylate.

Keywords: Free Radical Polymerization, Kinetics, Mechanism, Phase Transfer Catalyst, Rate of Polymerization.

Revolutionary and remarkable achievements were accomplished by the introduction of phase transfer catalysts (PTC) in the chemical industries. This distinct form of the heterogeneous catalyst has made tremendous changes in the mechanical facets of organic reactions[1] by transferring reactants present in two different phases. Exciting trends in achieving high-product yields, higher reaction rates with optimal reaction conditions,and the viability of reactions in the presence of water with minimal solvents have made significant changes in organic reactions. PTC has added its importance in heterocyclic chemistry, organometallic synthesis, pharmaceutical, agrochemical manufacture, and polymer chemistry[2]. The insolubility of water-soluble and cost-effective initiators in the organic solvents has limited their use in polymerization. The phase transfer catalyst's introduction alleviated the problem[3] effortlessly by unveiling the highly reactive species between the two immiscible organic/aqueous phases. Many researchers have investigated water-soluble initiators' efficiency by incorporating them for the polymerization of water-insoluble vinyl monomers accelerated by a phase transfer catalyst. The first report on crown ether (PTC) / potassium peroxydisulphate initiated free radical polymerization of *n*-butyl acrylate[4] was discussed in 1980. The kinetics of polymerization associated with acrylonitrile using potassium peroxomonosulphate as initiator and tetrabutyl phosphonium chloride as phase transfer catalyst was reported[5]. The influence of monomer concentration on polybutyl methacrylate in the presence of water soluble initiator as potassium peroxydisulphate and in the presence of cetyltrimethylammonium bromide as PTC was discussed[6]. Yoganand *et al.*[7], reported an increase in rate of polymerization with increase in concentration of cetyldimethylbenzylammonium chloride as PTC for methyl methacrylate but decrease in rate of polymerization for acrylonitrile. An increase in rate of polymerization was observed in the case of ultrasound assisted phase transfer catalystalong with water soluble initiator[8,9] compared to normal conditions. The effect of PTC on the rate of polymerization of vinyl monomers in the presence of water-soluble initiators was reported[10-12] by many researchers. In the present study, the efficacy of the water-soluble initiator - potassium peroxydisulfate in presence of single-site PTC - 2-Benzoylethyldecyldimethylammonium bromide and di-site PTC-1,1,4,4-Tetramethyl-1,4 dioctylethylenediammonium bromide,was investigated by polymerizing glycidyl methacrylate (GMA)and from its kinetics.

Experimental Section

Materials and Methods

Materials

Glycidyl methacrylate (GMA) (Merck, India) was distilled at reduced pressure before use, to remove the inhibitor. The water-soluble initiator, potassium peroxydisulfate (PDS), was purified by recrystallization (Merck, India) before use. Paraformaldehyde, acetophenone, hydrochloric acid, sulphuric acid, sodium bicarbonate, sodium bisulphate, *n*-bromodecane and dimethyl amine (Merck, India) were used as received.The solvents ether, acetone, ethyl acetate, cyclohexane, cyclohexanone, methanol and ethanol (SRL, India), were used as received. Doubly distilled water was used in the biphasic system as a solvent.

Synthesis of phase transfer catalysts

Synthesis of Single-site – PTC: 2-Benzoylethyl-decyldimethylammonium bromide

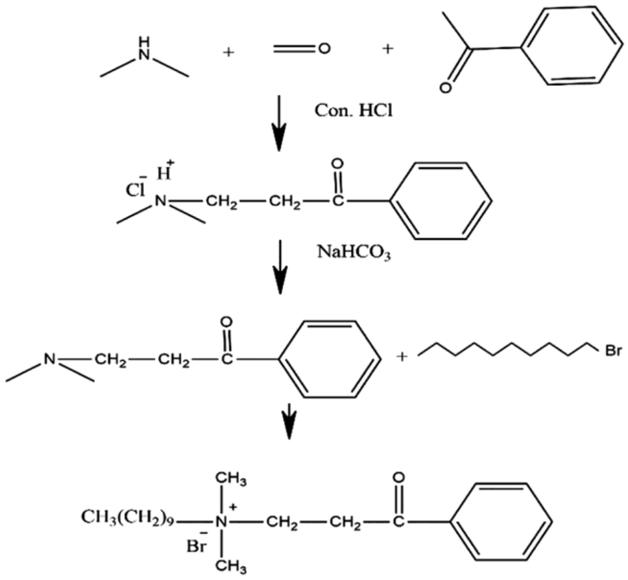
A single site phase transfer catalyst was prepared[12] as reported. Initially, dimethylaminepropiophenone hydrochloride was prepared[13] by placing equal moles of (0.3 mol) dimethyl amine and paraformaldehyde and 0.25 mol of acetophenone in a 250 mL round bottom flask. Then, this mixture was refluxed with ethanol and hydrochloric acid for 2 h. The homogenous solution was treated with acetone and allowed to cool overnight. The filtered dimethylaminepropiophenone hydrochloride crystals were recrystallized and used. In the second stage, 0.28 M of the prepared dimethylaminepropiophenone hydrochloride in ether was treated with 100 mL of sodium bicarbonate (0.1N) solution in a separation funnel. The ether layer containing the amine was quaternized by the addition of 0.28 mol of *n*-bromodecane in cold conditions. The obtained product was purified by recrystallization using acetone-alcohol mixture. After being dried in a vacuum, the purified 2-benzoylethyl-decyldimethylammonium bromide (BEDDAB) was collected (Scheme 1).

Synthesis of the Di-Site PTC: 1,1,4,4-Tetramethyl-1,4 dioctylethylenediammonium bromide

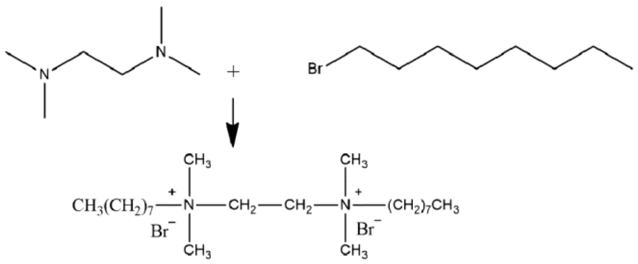
The di-site PTC was prepared[14] by introducing 0.01 mol of N,N,N’,N’-tetramethylethylenediamine in a 250 mL flask. To this, 0.02 mol of 1-bromooctane was added and temperature of 60ºC was supplied continuously to the reaction mixture with refluxing for 2h. The resulted white coloured 1,1,4,4-tetramethyl-1,4-dioctylethylenediammonium bromide (TDEDB) precipitate was filtered and used after purification using a minimal amount of acetone/ethanol (Scheme 2).

Polymerization of glycidyl methacrylate

Glycidyl methacrylate was polymerized using a thick-walled, long, airtight Pyrex tube under unstirred condition. An inert nitrogen atmospheric condition was maintained in the tube after de-aeration of oxygen, and the temperature was maintained as 60 ± 1°C using a thermostat. The monomer GMA was added to ethyl acetate (organic phase) In the Pyrex tube, 10 mL of ethyl acetate (organic phase) containing GMA and 10 mL of aqueous phase containing PTC(BEDDAB /TDEDB) along with sodium bisulfate (0.5 mol) to control the ionic strength, and sulfuric acid (0.2 mol) to regulate the *p*H level were taken. With careful addition of PDS to the biphasic medium, the polymerization reaction was initiated. The appearance of



Scheme 1 — Synthesis of 2-Benzoylethyldecyldimethylammonium bromide



Scheme 2 — Synthesis of 1,1,4,4-Tetramethyl-1,4 dioctylethylenediammonium bromide a precipitate indicates the polymerization of GMA. The reaction was arrested by pouring the reaction mixture onto ice-cold methanol[15] after a specified time.The newly synthesized polyglycidyl methacrylate (PGMA) was filtered using a G4 sintered glass crucible; it was washed repeatedly with double distilled water and methanol. The obtained PGMA was dried in an oven (60 ± 0.1°C) to achieve its constant weight. The same conditions were maintained except PTCs, and polymerization was executed. There was no evidence of formation of polymer except a slight colour change in the system. It implies the role of PTC in the polymerization of GMA (Scheme 3).

The rate of polymerization of GMA was calculated using equation (1):

$$\mathrm{Rp} = 1000\ \mathrm{W/V} * \mathrm{t} * \mathrm{M} \qquad \ldots (1)$$

where W is the weight of the PGMA in g, V is the volume of the reaction mixture in ml, t is the reaction time in seconds, and M is the molecular weight of monomer g/mol. The expected reaction mechanism of free radical polymerization of GMA in presence of water-soluble initiator and PTCs is depicted in the (Scheme 4).

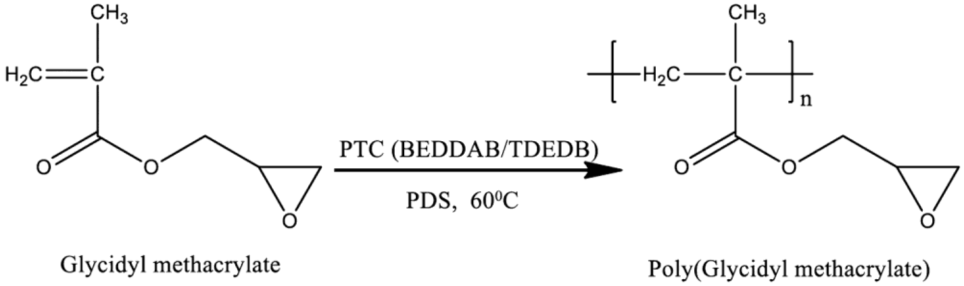
Results and Discussion

Steady-state rate of polymerization

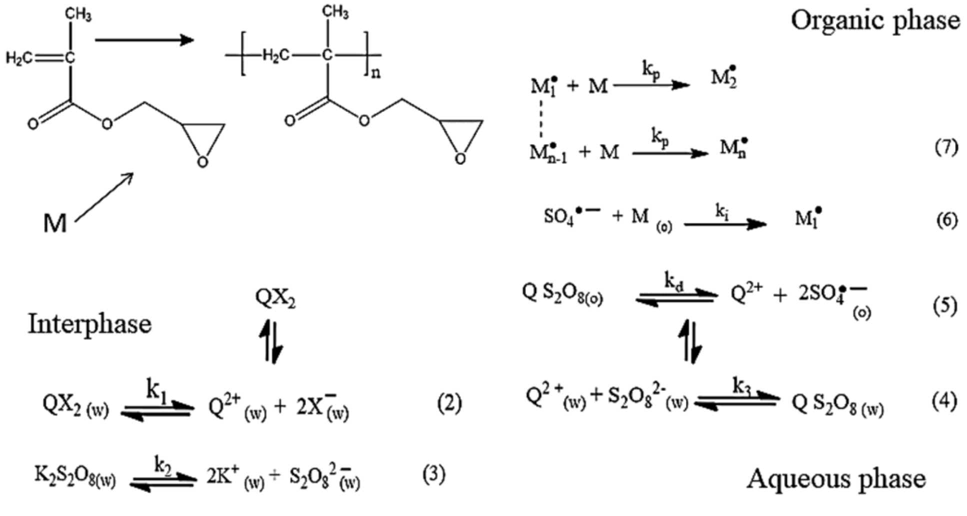
The steady-state of rate polymerization (Rp) for GMA, was determinedby keeping the monomer concentration as 2.0 mol.dm^{-3}, and PTC (BEDDAB and TDEDB) as 0.1 mol.dm^{-3} in a total volume (aqueous + organic phases) of 10 mL each; sulfuric acid (0.2 mol.dm^{-3}), and sodium bisulfate (0.5 mol.dm^{-3}) were also added to maintain ionic and acid strength as constant. The polymerization was initiated by adding 0.02 mol.dm^{-3} PDS. The initial sharp rise and after that a slight decrease with time was observed during polymerization. Based on the plot shown in Fig. 1, the steady-state rate for PGMA was fixed as 40 min, using both single and di-site PTC.

Influence of monomer concentration on the rate of polymerization

To find the effect of monomer concentration on the rate of polymerization (Rp), monomer concentration was varied from 0.8 to 1.8 mol.dm^{-3} and PDS and PTC (BEDDAB and TDEDB) concentrations were maintained as 0.02 mol.dm^{-3} and 0.1 mol.dm^{-3} respectively. The reaction mixture was maintained at



Scheme 3 — Phase transferred catalyzed radical polymerization of GMA



Scheme 4 — Travel path of PTC in GMA – BEDDAB/TDEDB – $K_2S_2O_8$ system constant ionic strength by adding 0.5 mol. dm^{-3} sodium bisulphate and constant *p*H by adding 0.2 mol.dm^{-3} sulphuric acid. An increase in Rp, with an increase in monomer concentration was observed. The order of the reaction was evaluated by plotting a graph (Fig. 2a) between 3+log [GMA] and 6+log[Rp]. Based on the plot, it was found to be around 0.9. The order of the reaction was found to be unity[16,17] with respect to the monomer. Figure 2b shows the plot of Rp as a function of monomer concentration raised to 0.9 is a straight line while polymerizing the GMA using both BEDDAB and TDEDB and lines passed through the origin; these plots confirm the above observations with respect to variation in [GMA]. Moreover, the R^2 value is also almost 9, which shows the large positive association of the points.

In the present case, Rp was found to be higher for the reaction polymerized with disite-TDEDB[18] because it provides two free anionic free radicals when compared to single site - BEDDAB, which can provide only one, hence at a time more number of propagating chains can be seen in di-site polymerization.

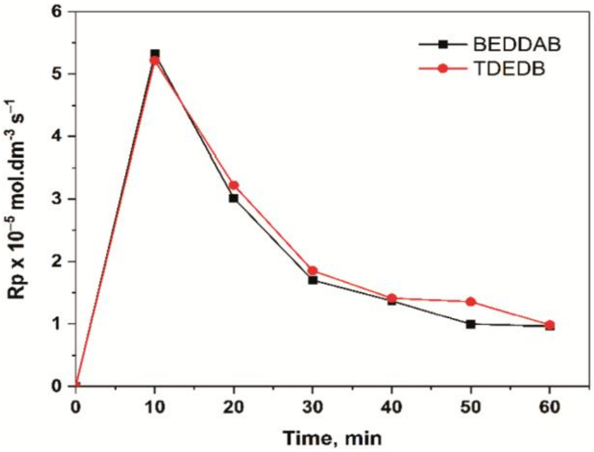


Fig. 1 — Steady state polymerization rate for PGMA

Effect of initiator concentration on the rate of polymerization

In order to find the impact of initiator on Rp, PDS concentration was varied from 0.015 M to 0.025 mol.dm^{-3} and concentrations of PTCs (0.1 mol.dm^{-3}), monomer (2 mol.dm^{-3}), sodium bisulphate (0.5 mol.dm^{-3}) and sulphuric acid (0.2 mol.dm^{-3}) was fixed as specified. Rp was found to increase with rise in concentration of initiator. The order of the reaction was found to be 0.5, based on the plot (Fig. 3a) of log Rp versus log [PDS]. The plot of Rp versus [PDS] raised to power 0.5 (Fig. 3b) passes through the origin and thus supports the above observation.

The order with respect to the initiator is found to be the square root of the initiator concentration[19] in most of the free radical polymerization of vinyl monomers, whenever the polymer radical terminates by the mutual bimolecular reaction. Moreover, the R-squared value is between 0 and 1, which shows the perfect positive linear association with the trend line. By varying the initiator's concentration, higher Rp was noted with di-site PTC when compared to single site PTC.

Effect of concentration of PTCs (BEDDAB and TDEDB) on the rate of polymerization

To determine the impact of PTCs on the rate of polymerization, it was varied in the concentration range of 0.015–0.025 mol.dm^{-3}, keeping all other factors as constant. The plot of log Rp vs. log [PTCs] was observed as linear with a slope of 0.5 (Fig. 4a), signifying half-order dependence. The plot of Rp vs. [PTCs] raised to the power 0.5 is linear as in Figure 4b and the lines pass through the origin, which supports the above observation. However, in the case of BEDDAB, we observed a slight decrease in Rp at a higher concentration. The decrease in Rp may be due to a bulky benzyl group of catalyst; Thus, a leveling of tendency at higher concentrations of catalyst was

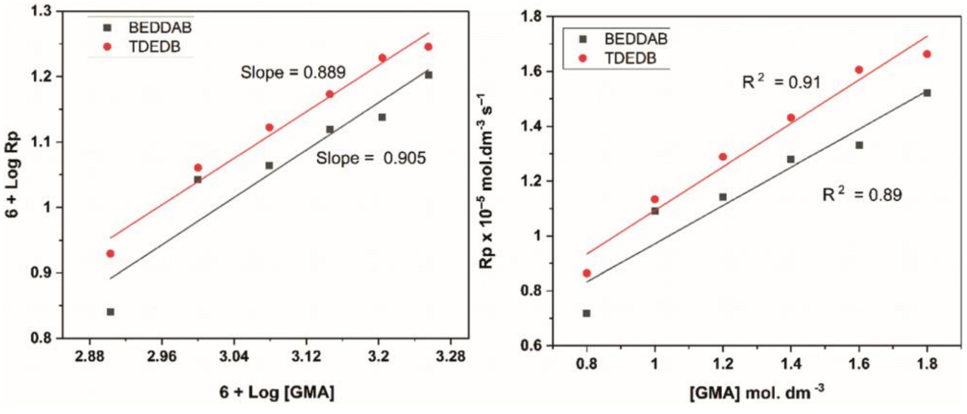


Fig. 2 — Plot of Rp Vs. [GMA] mol. dm-^{3}

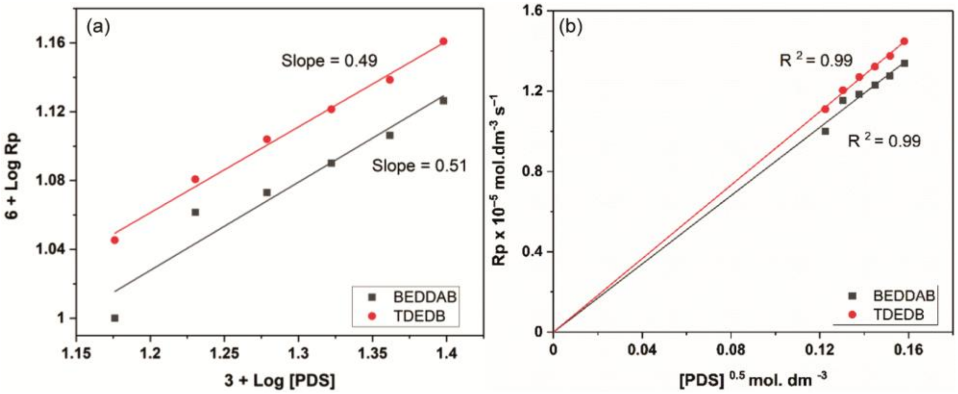


Fig. 3 — Plot of Rp Vs. [PDS] $^{0.5}$ mol. dm-^{3}

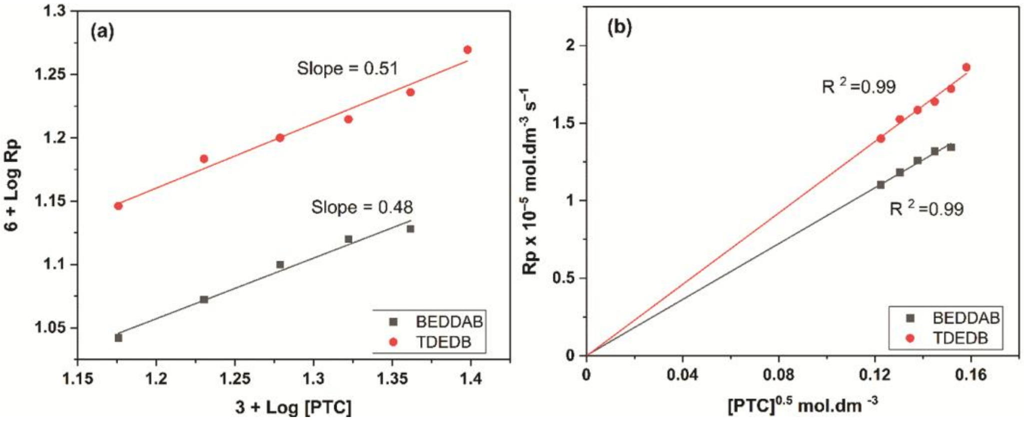


Fig. 4 — Plot of Rp Vs [PTC] $^{0.5}$ mol. dm-^{3}

observed. The same trend at higher concentrations of PTC was reported in the literature[20]. At the same time, the same trend of higher Rp was noticed with TDEDB compared to BEDDAB.

Dependence of ionic strength

The rate of polymerization was determined by varying ionic strength (μ) in the range from 0.4 to 0.6 mol.dm^{-3} by maintaining the concentrations of monomer, initiator, PTCs and *p*H as constant. Though it was varied in the specified range, there were no significant changes (Table 1) in the polymerization rate[21].

Effect of *p*H

To determine the role of *p*H on the rate of polymerization, it was varied in the range of 0.1 to 0.3 mol dm^{-3} by keeping all other parameters as constant. The rate of polymerization was not influenced by variation (Table 2) in the concentration[22]

Influence of solvent polarity on the rate of polymerization

The polar solvents, namely cyclohexane, ethyl acetate, and cyclohexanone, with three different dielectric constants 2.02, 6.02, and 18.03 were selected to find its impact on the rates of polymerization. Figure 5 shows the increase in trend of Rp, as the dielectric constant of the solvents increases. As the solvent polarity increases, there is an ease in movement of sulfate ions into the organic phase, hence the Rp increases[23].

Table 1 — Effect of μ on rate of polymerization

[μ] mol.dm^{-3}	Rp × 10^{-5} mol.dm^{-3}.s^{-1} BEDDAB	Rp × 10^{-5} mol.dm^{-3}.s^{-1} TDEDB
0.40	1.3562	1.3962
0.45	1.3574	1.3973
0.50	1.3595	1.4001
0.55	1.3603	1.4075
0.60	1.3638	1.4094

Table 2 — Effect of [H]$^{+}$ on rate of polymerization

[H]$^{+}$ mol.dm^{-3}	Rp × 10^{-5} mol.dm^{-3}.s^{-1} BEDDAB	Rp × 10^{-5} mol.dm^{-3}.s^{-1} TDEDB
0.10	1.3587	1.3989
0.15	1.3632	1.4013
0.20	1.3661	1.4089
0.25	1.3682	1.4113
0.30	1.3694	1.4176

Effect of temperature on the rate of polymerization

The performance of polymerization can be validated by another prime factor that is temperature.

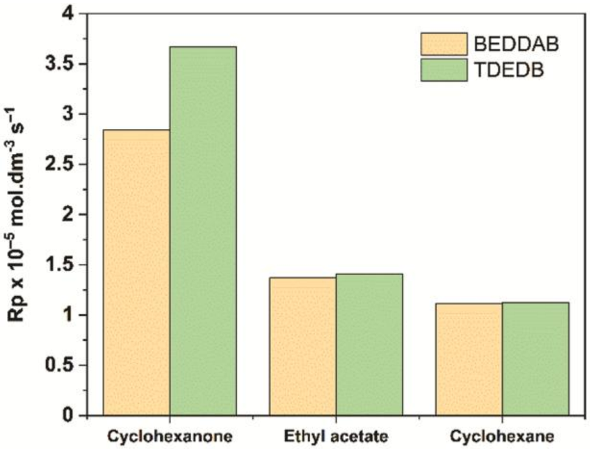


Fig. 5 — Plot of Rp Vs. Polar solvents

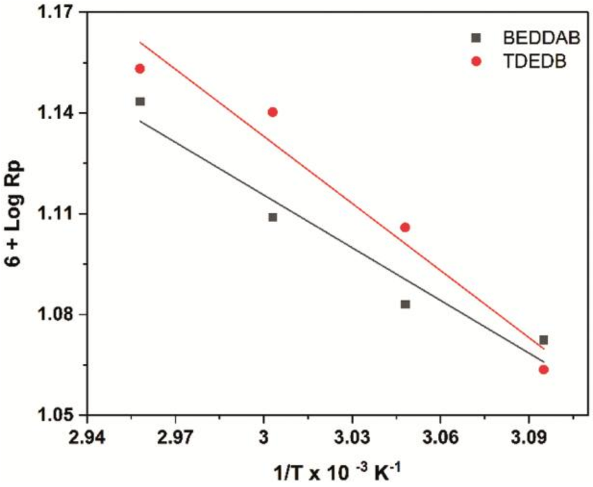


Fig. 6 — Effect of temperature on Rp

To find the influence of temperature, the temperature was increased from 50ºC to 60ºC and Rp was determined for every 5ºC rise by keeping all other parameters like concentrations of monomer, initiator, acid, and ionic strengths as constant. As the temperature increased, Rp was also found to increase. The increase in temperature initiates more number of formation of free radicals from the initiator[24], thus an increase in active sites and hence an increase in the rate of polymerization. From the Arrhenius plot (Figure 6), the thermodynamic characteristics like overall activation energy, Ea of polymerization of GMA, –enthalpy of activation ($\Delta H^{\#}$), free energy of activation ($\Delta G^{\#}$), entropy of activation ($\Delta S^{\#}$) were calculated and presented in Table 3.

In this, though, the activation energy of BEDDAB is less than TDEDB and Rp of TDEDB was higher. The activation energy in the case of BEDDAB is lower probably because the complex PTC-radical to be transferred in the organic phase contains only one ionic center, unlike the case of TDEDB.

Table 3 — Thermodynamic parameters for polymerization of GMA – BEDDAB/TDEDB – $K_2S_2O_8$

PTC	*Ea, kJmol^{-1}	**$\Delta H^{\#}$, kJmol^{-1}	$\Delta S^{\#}$, eu	$\Delta G^{\#}$, kJmol^{-1}
BEDDAB	10.02	7.27	-164.47	61.98
TDEDB	12.75	10	-155.93	61.92

*Ea was determined usingArrhenius equation, $k = Ae^{(-Ea/RT)}$ where k is the rate constant, A is preexponential factor, Ea is the activation energy, R is universal gas constant and T is absolute temperature in K.
** ΔH, ΔSand ΔG were calculated based on Erying's equation

Mechanism of GMA in ethyl acetate/water biphasic medium

The free-radical polymerization of GMA was carried out in ethyl acetate/water biphasic system, initiated by $K_2S_2O_8$ and BEDDAB and TDEDB[25]as catalysts. The following results were obtained from the kinetic study.

- The reaction exponent with respect to [monomer] = 1.
- The reaction order with respect to [$K_2S_2O_8$] = 0.5.
- The reaction order with respect to [PTCs] = 0.5.
- Rp increased with an increase in solvent polarity.
- The rate of polymerization was independent of ionic strength (μ) and [H^+].

A lucid mechanism (Scheme 4) was proposed to explain the observations based on the experimental values. The subscripts (w) and (o) denotes aqueous and organic phases, respectively, while k_1, k_2, and k_3 are equilibrium constants of equations (2) to (4); k_d is the dissociation constant of equation (5); k_i, k_p, and k_t are the rates of initiation, propagation, and termination, respectively, and QX_2 represents the PTC. Scheme 4 depicts the dissociation of PTC and PDS in aqueous phase and initiation and formation of PGMA in organic phase, and the same are represented from equations from 2-7.

The equilibrium constants k_1, k_2 and $k_3$of initiation, propagation, and termination reaction can be given as

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

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

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

The rate of initiation, R_i from equation (5) for the sulphate ion free radical is represented as

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

Where f, is the initiator efficiency;

Rate of propagation from equation (7) can be represented as

$$\bullet \qquad \ldots (12)$$

$$\bullet \qquad \rule{2em}{0.4pt} \qquad \ldots (13)$$

Termination of polymer in radical polymerization occurs by colliding two propagating chains and is represented as

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

The rate equation for termination can be given as

$$\bullet \qquad \ldots (15)$$

At the steady-state, the rate of initiation is equivalent to the rate of termination, i.e.

$$R_i = R_t \qquad \ldots (16)$$

From equation (11) and (15)

$$\bullet \qquad \ldots (17)$$

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

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

From equation (12) and (19)

$$R_p = k_p \left[\frac{k_d f k_3}{k_t}\right]^{1/2} [Q^{2+}]^{0.5} [S_2\ O_8{}^{2-}]^{0.5} \quad \bullet \qquad \ldots (20)$$

The above-derived expression sufficiently explains all the experimental observations of GMA's polymerization in the presence of PTCs (BEDDAB/TDEDB) using the water-soluble initiator, $K_2S_2O_8$.

Conclusion

The monomer GMA was polymerized by employing single-site PTC – BEDDAB and di-site PTC – TDEDB in the presence of water-soluble initiator $K_2S_2O_8$. After determining the steady rate of polymerization as 40 min, a kinetic study was carried out by varying the concentration of monomer, initiator, PTCs, ionic and acid strengths, and temperature. However, at the same time, a unique leveling of tendency was noted while polymerizing GMA with BEDDAB due to the catalyst's bulky benzyl group. Apart from this, in all other parameters, the present kinetic study followed the general kinetics of polymerization. The influence of solvent polarity revealed that the increase in the dielectric constant of the solvents increases the polymerization rate. At the same time, on comparison of prepared single and di-site PTCs, the rate of polymerization was higher in the case of di-site PTC when compared to single-site PTC. Thus, the kinetic study reveals that if multi-site PTC is employed for the polymerization reaction or other organic reactions, the rate may be enhanced and which could be a potential interest for many immiscible reactions.

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