Synergetic effect of multi-site phase transfer catalysis system mediated free radical polymerization of acrylonitrile – a kinetic study

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ABSTRACT

In this work, the kinetics and mechanism of free radical polymerization of acrylonitrile (AN) using potassium peroxydisulphate (PDS-$K_2S_2O_8$) as a water soluble initiator in the presence of synthesized 4,4'-dihexadecyl-1,1'-bipyridine diiumdichloride (DHBPDDC) as multi-site phase-transfer catalyst (MPTC) has been investigated. The polymerization reaction were carried out under nitrogen atmosphere and unstirred condition at constant temperature $60\pm1°C$ in ethyl acetate/water biphasic medium. The effects of variation of monomer (AN), initiator (PDS) and catalyst (MPTC) solvent polarity and temperature on the rate of polymerisation (Rp) were ascertained. The order with respect to monomer (acrylonitrile) was found to be unity. The order with respect to initiator and catalyst was found to be 0.51, 0.48 respectively. However, an increase in the polarity of the solvent has slightly increased the rate of polymerization value (Rp). Based on the results obtained, a suitable kinetic mechanism scheme has been proposed to account for the experimental observations and its significance was discussed. The other thermodynamic parameters such as entropy of activation (($\Delta S^{\#}$), enthalpy of activation ($\Delta H^{\#}$) and free energy of activation ($\Delta G^{\#}$) have been calculated.

1. Introduction

The phase – transfer catalysts usually as quaternary onium salts, crown ethers, cryptands etc., can be applied to give a high change and products selectivity. Phase-transfer catalysis is considered to be one of most well-organized tools in all branches of chemistry because of its ease, high conversion, under very mild reaction condition and environmental concern [1-4]. It is widely used for manufacturing pharmaceuticals, agricultural chemicals, perfumes, flavours, dyes, polymers and environmental applications. The reaction between mutually immiscible reactants was usually difficult to conduct strongly even under severe operating. Such problems as low reaction rate, low conversion of reactants and low of products can be overcome by phase-transfer catalysis (PTC) [5–8]. Many authors reported the single-site PTC assisted radical polymerization of hydrophobic vinyl monomers in aqueous-organic two phase system [9-12]. Recently, the catalytic behaviour of multi-site phase-transfer catalysts has been attracted much attention, due to the fact that multiple molecules of the aqueous reactant can be carried into the reaction phase once a reaction cycle. The catalytic competence is thus better [13-16]. The first report published on multisite PTC (MPTC) was by Idoux et al., and they have synthesized phosphonium and quaternary onium ions containing more than one site per molecule [17].Vajjiravel et al [18-19] reported the kinetics of free radical polymerization of vinyl

monomers using multisite PTC-PDS system in organic-water two phase medium. The phase-transfer catalyzed free-radical polymerization of vinyl monomers with water-soluble initiators like potassium peroxydisulphate (PDS) and ammonium perdisulphate (ADS) is a relatively new area of research [20]. It has been found that such water soluble initiators have been used efficiently for bulk or solution polymerization with phase-transfer catalysts [21-23]. A several authors reported the use of single site-PTC for free radical polymerization of vinylic monomers in aqueous organic two phase medium such as butylacrylate (BA), methyl methacryate (MMA), methacrylate (MA), glycidyl methacrylate (GMA), Butyl methacrylale, ethyl methacrylate (EMA) [24-30] etc. The review of literature on this method reveals that, so far, very few reports are obtainable in free radical polymerization of vinyl esters under MPTC condition. Kinetics of polymerization ortho-, meta-, and para-tolymethacrylates and $K_2S_2O_8$/TBBA (tetra butyl ammonium bromide) – assited free –radical polymerization [31-32]. Systematic literature survey reveals that no symmetric investigation of the kinetics and mechanism of polymerization of acrylonitrile (AN) with initiator ($K_2S_2O_8$) and synthesized 4,4'-dihexadecyl-1,1'-bipyridine diium dichloride (MPTC) (**Scheme 1**) has been carried out.

The prompted us to undertake the current study which deals with the kinectics of free radicals polymerization of AN in unstirred ethyl acetate/water mixture using $K_2S_2O_8$ as the initiator and multisite phase transfer catalyst system.
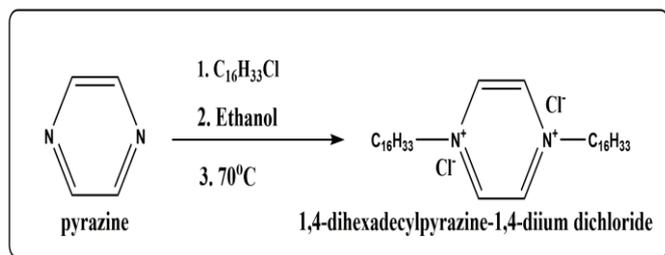
Scheme 1. Synthesis of Multi-site phase-transfer catalyst

2. Experimental Methods
2.1. Materials and equipments

Acrylonitrile (Merck, Mumbai, India) was washed with 5% NaOH solution to remove the inhibitor and with double distilled water to remove the basic impurities and then dried over calcium chloride and distilled under reduced pressure. The initiator Potassium peroxydisulphate (Nice, India), 4, 4'-bipyridine (CDH, New Delhi, India), 1-hlorohexadecane (Aldrich, USA), ethyl acetate (CDH, New Delhi, India) and methanol (SRL, Mumbai, India) were used as received. The FT-IR spectra were recorded on a Bruker-Tensor 27 FT-IR spectrophotometer. The ^{1}H NMR and ^{13}C NMR spectra

were recorded on Bruker 400 and 100 MHz spectrometer using TMS as an internal standard and D_2O as the solvent. Elemental analysis was performed on a Perkin–Elmer 240B elemental analyzer.

2. 2. Synthesis of a multi-site phase transfer catalyst

The water- soluble multi-site phase transfer catalyst (MPTC) was synthesized in one step. A mixture of 1g (12.48 mmol) of 4,4'-bipyridine, 7g (24.96mmol) of 1-chlorohexadecane and 75 mL of ethanol was placed in a 250 mL three-necked round bottomed Pyrex flask. The reaction was carried out at 70°C for 48 hours and was gently refluxed in the nitrogen atmosphere. The solvent was then completely removed under vacuum and the onium salt, i.e. 4,4'-dihexadecyl-1,1'-bipyridine diium dichloride (MPTC) was washed with ether. The white solid catalyst was stored in a $CaCl_2$ desiccator.

^{1}H NMR (400 MHz, D_2O): δ_H. 9.04-8.87(dd,J=4.6Hz,6H), 8.59-8.47(dd,J=5.05Hz,6H), 4.75-4.69(m,46H), 2.17-2.08 (m,4H), 1.39-1.29(m,51H), 0.89-0.87(t, J=2.55Hz,6H)

^{13}C NMR (100 MHz, D_2O):

δ 146.82,125.52,124.85,121.99,60.43,29.50,26.69,23.74,20.52,11.95

Elemental analysis: Calculated: C, 71.84; H, 11.72; Cl, 11.78; N, 4.65; and Found: C, 71.63; H, 11.59; Cl, 11.70; N, 4.55%.

2.3. Polymerization Procedure:

The polymerization reactions were carried out in an inert atmosphere at 60$\pm$1°C. The reaction mixture consists of 10 mL of aqueous phase and 10 mL of organic phase. The monomer in ethyl acetate solvent was the organic phase. The catalyst, potassium sulphate (for adjusting ionic strength) and sulphuric acid (for maintaining (H$^+$) were taken in the aqueous phase. The reaction mixture was thoroughly desecrated for 30 min. when potassium peroxydisulphste(PDS) was added to the reaction mixture, polymerization started and polyacrylonitrile precipitated continuously during polymerization without stirring or agitation. The polymerization reactions were arrested by pouring reaction mixture into ice-cold methanol containing traces of hydroquinone. The polymer formed was filtered quantitatively through a sintered crucible (G-4), washed five times with distilled water and methanol, dried in a vacuum oven at 50-60°C in a vacuum oven to constant weight (**Scheme 2**). The rate of polymerization (Rp) was calculated from the weight of the polymer formed. Rp was calculated from the weight of polymer obtained using the following formula [34]:

$$R_P = \frac{1000W}{V \times T \times M}$$

where,

W– weight of the polymer in gram.

V – volume of the reaction mixture in mL.

T – reaction time in seconds.

M – molecular weight of the monomer AN

PTC is able to transferring the reactants of aqueous phase into organic phase, where the reaction will take place. In this aqueous–organic bi-phase medium, the reaction of QX (phase transfer catalyst) and KZ (initiator) in the water phase produces QZ at the interface between the two phases where it was decomposed and produced the radical ions which initiate the polymerization reactions at 60 ± 1 C. The simple representation of this process is shown in (**Scheme 3).**

3. Results and discussion

The polymerization of acrylonitrile initiated by potassium peroxydisulphate (PDS) in aqueous medium was studied under different experimental conditions to evaluate the various parameters, which influence the polymerization reaction.
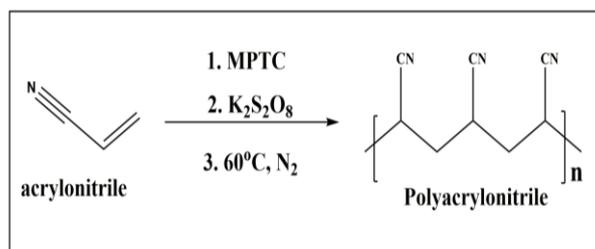
Scheme 2. Polymerization of acrylonitrile
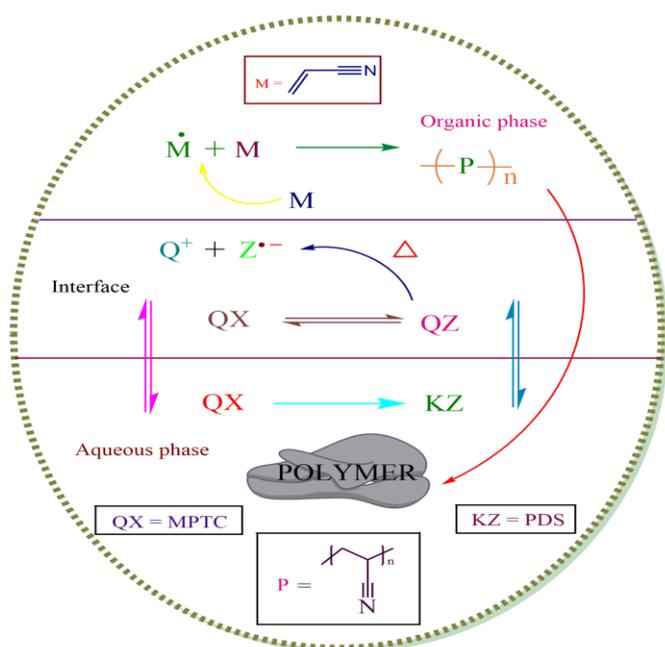
Scheme 3. Simple representation reaction model for polymerization of AN

3.1. Steady state rate of polymerization

The steady state rate of polymerization was ascertained by carrying out the polymerization of the monomer (acrylonitrile) at different time intervals keeping the concentrations of monomer, initiator, MPTC, and pH constant. The plot of Rp versus time shows a sharp increase to some extent, then slightly decreased and thereafter remains constant. The time taken was found to be 30 min (Table 1, Fig.1).
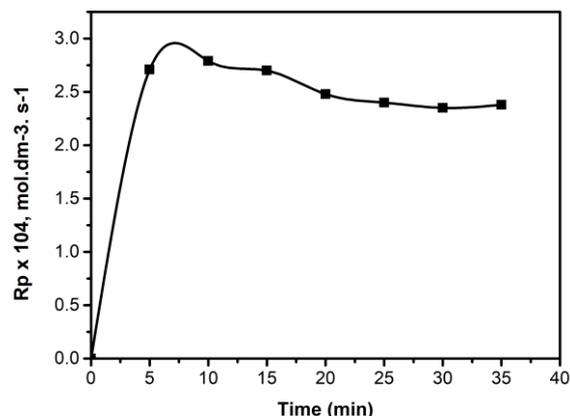
Fig. 1. Steady state rate of polymerization: Reaction condition: [AN], 2.5 mol dm^{-3};[K$_2$S$_2$O$_8$],2.0 x10^{-2} mol dm^{-3}; [MPTC], 2.0 x10^{-2} mol dm^{-3}; [H$^+$], 0.2 mol dm^{-3}; [μ], 0.05 mol dm^{-3}; Temp, 60°C.

Table 1. Steady State rate of Polymerisation: Reaction condition: [AN], 2.5 mol dm^{-3};[K$_2$S$_2$O$_8$],2.0 x10^{-2} mol dm^{-3}; [MPTC], 2.0 x10^{-2} mol dm^{-3}; [H$^+$], 0.2 mol dm^{-3}; [μ], 0.05 mol dm^{-3}; Temp, 60°C

Time (min)	Rp x 10^4 mol dm^{-3} s^{-1}
5	2.71
10	2.79
15	2.70
20	2.50
25	2.48
30	2.40
35	2.35

3.2. Effect of [MPTC] on Rp

The dependence of Rp on the concentration of MPTC was examined by varying MPTC in the range 0.01–0.08 mol dm^{-3} at fixed concentrations of monomer, PDS, pH and ionic strength. A plot of (5 + log Rp) vs 3+log [MPTC], was found to be linear with a slope 0.48. The plot of Rp vs [MPTC] passing through origin confirms the above observations (Fig. 2a,b). The increase in Rp value is attributed to the change in the size, surface area and morphology of MPTC due to the positive effect. Further, the collision between intermediates [QS$_2$O$_8$] is increased by increasing MPTC amount. Therefore the opportunity of forming a complex between them is largely increased. Hence, the Rp increased with increase in the amount of MPTC. Choi and Lee [33] reported the kinetics of bulk (free-radical) polymerization of methyl methacrylae (MMA) with the PDS - 18-crown-6 system.
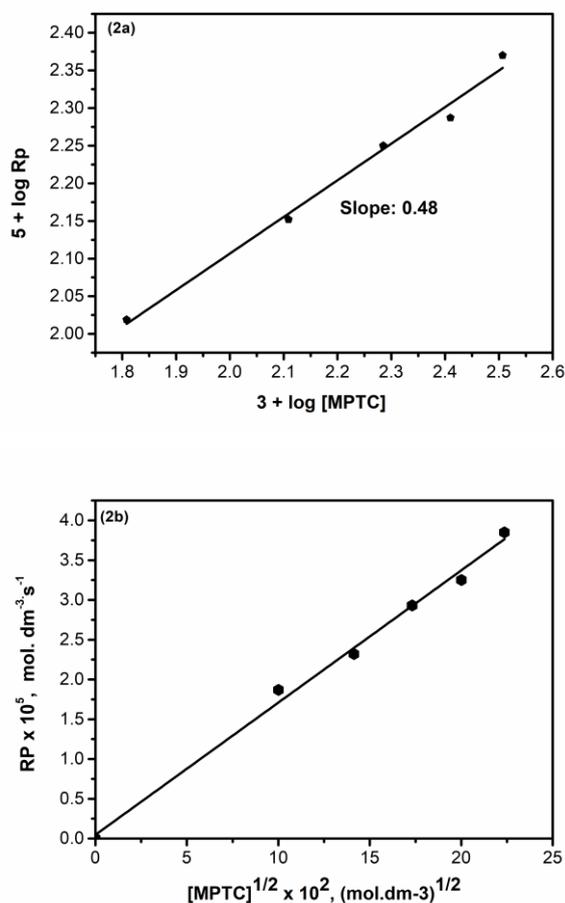
Fig. 2a,b. Effect of [MPTC] on Rp: Reaction condition: [AN], 2.5 mol dm^{-3};[K$_2$S$_2$O$_8$], 2.0 x10^{-2} mol dm^{-3}; [MPTC], 2.0 x10^{-2} mol dm^{-3}; [H$^+$], 0.2 mol dm^{-3}; [μ], 0.05 mol dm^{-3}; Temp, 60°C, 30min.

3.3. Effect of initiator concentration on Rp

The polymerization rate increased with increased concentration of PDS in the range 0.01–0.08 mol dm^{-3} a fixed concentration of MPTC, pH, and monomer. A plot of 5 + log Rp vs 3+ log [PDS] was found to be linear

with a slope of 0.51. The plot of Rp vs [PDS] is linear passing through the origin supporting the above deduction (Fig. 3a,b.). The square-root dependency of Rp on [K$_2$S$_2$O$_8$] in the polymerization of acrylonitrile suggests that the induced decomposition of QS$_2$O$_8$ is present and that the polymer radicals terminate by the mutual bimolecular reaction. It implies that the formation of QS$_2$O$_8$ between PDS and MPTC may be enhanced. The formed S$_2$O$_8$ is more lipophilic and hence it easily entered into the organic phase from the aqueous phase where contain monomer. Therefore the monomer and QS$_2$O$_8$ are reacting rapidly and form polymer [34-36].
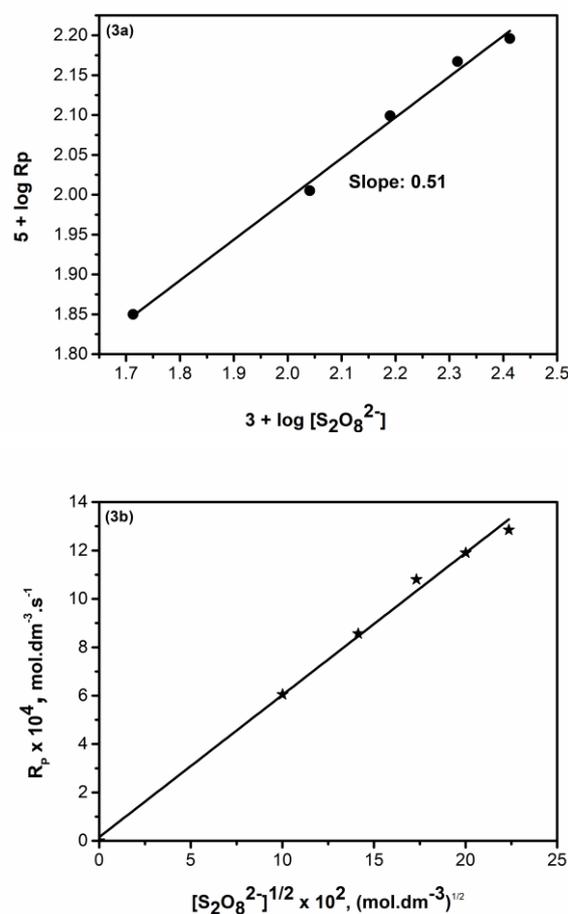
Fig. 3a,b. Effect of initiator concentration on Rp: Reaction condition: [AN], 2.5 mol dm^{-3};[K$_2$S$_2$O$_8$],2.0 x10^{-2} mol dm^{-3}; [MPTC], 2.0 x10^{-2} mol dm^{-3}; [H$^+$], 0.2 mol dm^{-3}; [μ], 0.05 mol dm^{-3}; Temp, 60°C, 30min.

3.4. Effect of monomer concentration on Rp

The effect of monomer concentration Rp was studied by varying the concentration in the range 0.37–1.28 mol dm^{-3} at fixed concentrations of PDS, MPTC, pH and at constant ionic strength. From the plot of (5 + log Rp) vs (3 + log [AN]), the order of the reaction with respect to monomer concentration is found to be 1.04 almost unity. The plot of Rp against [AN] passing through the origin confirms the above observations (Fig. 4a, b.). A similar order of unity has been observed by many other authors

[37] in the phase-transfer catalyst assisted polymerization of vinylic monomers using $K_2S_2O_8$ as the initiator. In our liquid–liquid biphase polymerization system, the synthesized poly glycidyl methacrylate (PGMA) the glycidyl group, particularly the cyclic ether group did not cleave, which is confirmed by FT-IR i.e., there is no OH, carbonyl, C=C stretching observed.

energy of activation ($\Delta G^{\#}$) have been calculated using Eyring plot (log R_p/T vs 1/T).

Ea kJ / mol	$\Delta G^{\neq}$ kJ /mol	$\Delta H^{\neq}$ kJ /mol	$\Delta S^{\neq}$ kJ / mol
81.94	32.33	74.56	- 96.88

Table 2. Thermodynamic parameters : Reaction condition: [AN], 2.5 mol dm^{-3};[$K_2S_2O_8$],2.0 $\times 10^{-2}$ mol dm^{-3}; [MPTC], 2.0 $\times 10^{-2}$ mol dm^{-3}; [H^+], 0.2 mol dm^{-3}; [μ], 0.05 mol dm^{-3}; Time, 30min.
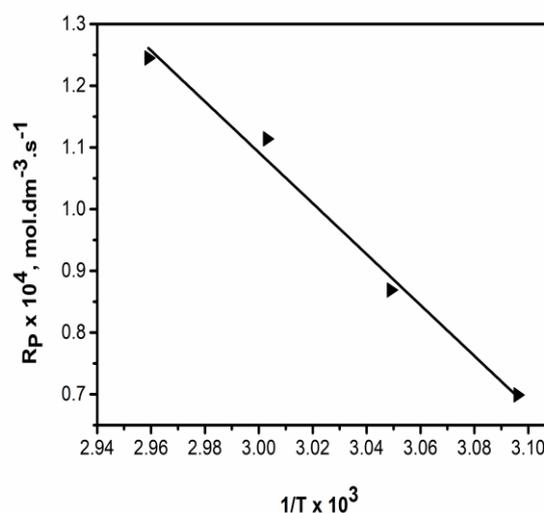
Fig. 5. Effect of temperature on Rp: Reaction condition: [AN], 2.5 mol dm^{-3};[$K_2S_2O_8$],2.0 $\times 10^{-2}$ mol dm^{-3}; [MPTC], 2.0 $\times 10^{-2}$ mol dm^{-3}; [H^+], 0.2 mol dm^{-3}; [μ], 0.05 mol dm^{-3}; 30min.

3.6. Effect of solvent on Rp

The effect of solvent on Rp was determined by carrying out the polymerization reaction of AA in six different solvents such as cyclohexane, ethyl acetate, cyclohexanone, toluene, benzene and chlorobenzene under a condition. It was found that the Rp decreased in(Table 3) the following order:

Cyclohexanone > ethyl acetate > chlorobenzene> toluene > benzene > cyclohexane

The decrease in the rate of polymerization may be due to the increase in the polarity of the medium, which facilitates the greater transfer of QS_2O_8 to the organic phase. The effect of the organic solvents on the rate of polymerization. Usually, the dielectric constants are used as the main index in choosing an appropriate organic solvent. The main reason is that the effect of the organic solvent involves the solubility of the catalyst, transition state of the reaction, ion transfer, salvation

Fig. 4a,b. Effect of monomer concentration on Rp Reaction condition: [AN], 2.5 mol dm^{-3};[$K_2S_2O_8$],2.0 $\times 10^{-2}$ mol dm^{-3}; [MPTC], 2.0 $\times 10^{-2}$ mol dm^{-3}; [H^+], 0.2 mol dm^{-3}; [μ], 0.05 mol dm^{-3}; Temp, 60°C, 30min.

3.5. Effect of temperature on Rp

The effect of variation of temperature in the range of 60° ± 1°C on the polymerization was studied by keeping other variables constant. The Rp increases with the increase in temperature. It is obvious that the reactivity is increased with an increase in the temperature. The reason is that the number of reactant molecules which possess higher activation energy at higher temperature. The collision of the reactants at a higher temperature is also increased. Hence, the Rp is increased at a higher temperature. From the slope of Arrhenius plot of 5 + log Rp vs 1/T (Table. 2, Fig. 5), the activation energy (Ea) value for the polymerization reaction was calculated. The other thermodynamic parameters such as entropy of activation (($\Delta S^{\#}$), enthalpy of activation ($\Delta H^{\#}$) and free

and interfacial phenomena which are difficult to determine to a phase-transfer catalyst system.

Solvents	Dielectric constant	$R_p \times 10^4$ mol dm^{-3} s^{-1}
Cyclohexanone	18.3	3.50
Chlorobenzene	5.70	3.18
Ethyl acetate	3.91	2.67
Toluene	2.50	2.35
Benzene	2.40	2.13
Cyclohexane	1.13	2.08

Table 3. Effect of solvent polarity on Rp: Reaction condition: [AN], 2.5 mol dm^{-3};[$K_2S_2O_8$],2.0 x10^{-2} mol dm^{-3}; [MPTC], 2.0 x10^{-2} mol dm^{-3}; [H^+], 0.2 mol dm^{-3}; [µ], 0.05 mol dm^{-3}; Time, 30min.

4. Mechanism and rate law

In the present investigation, Potassium perdisulphate (PDS) as the water soluble initiator, is migrated from the aqueous phase to the monomer containing organic phase is facilitated by the name (MPTC) which serves as the phase transfer agent. Rasmussen and Smith [38] studied that the presence of 18-crown-6 and quaternary salts ammonium salts as the phase transfer agent accelerate the rate of transfer of PDS from the aqueous phase to the monomer phase. They also observed that the formation of quaternary peroxydisulphate complex ($Q_2S_2O_8$), which was soluble in the organic medium, was responsible for the rapid polymerization of monomers like methyl methacrylate [39] .Thus the quaternary ammonium salts transfer the PDS ion from aqueous phase to organic phase and enhance the rate of decomposition of $S_2O_8^{2-}$ to sulfate ion radicals which initiates the polymerisation. Based on the kinetic results the following mechanism was proposed for the polymerization of AN. The following reactions characterizing the polymerization of Acrylonitrile (M) initiated by $K_2S_2O_8$ / MPTC in ethyl acetate/ water two- phase systems. It is assumed that dissociation of quaternary salt QX and $K_2S_2O_8$, the formation of QS_2O_8 in aqueous phase, and initiation of monomer in organic phase occurs by the following reactions.

(a) Phase Transfer

$$Q^{2+} + S_2O_8^{2-} \xrightarrow{k_1} Q S_2O_8^{2-} \tag{1}$$

(b) Initiation

$$QS_2O_8 \xrightarrow{k_d} Q^{2+} + 2SO_4^{\bullet-} \atop (o) \tag{2}$$

$$SO_4^{\bullet-} + \overset{\bullet}{M}_{(o)} \xrightarrow{k_i} M_1 \tag{3}$$

(c) Propagation

$$\overset{\bullet}{M}_1 + M \xrightarrow{k_p} \overset{\bullet}{M}_2 \tag{4}$$

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$$............$$

$$\overset{\bullet}{M}_{n-1} + M \longrightarrow \overset{\bullet}{M}_n \tag{5}$$
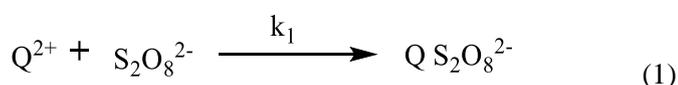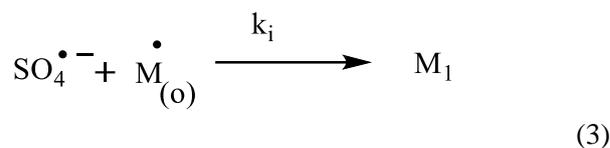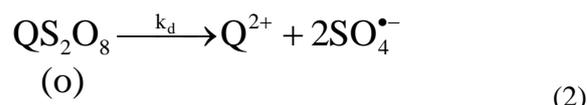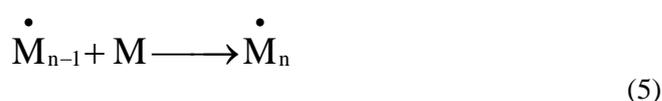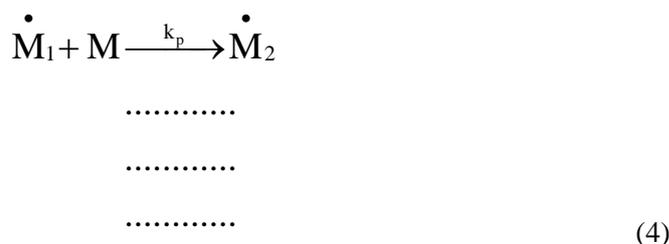
(d) The termination occurs by the combination of two growing polymer chain radicals, it can be represented as

$$2\overset{\bullet}{M}_n \xrightarrow{k_t} polymer \tag{6}$$
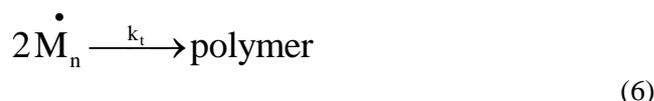
(Poly Acrylonitrile)

The subscripts (o) and (w) refer to organic phase and aqueous phase respectively.

Applying the general aspects of free radical polymerization and stationary state hypothesis to the radical species, the rate law for this mechanism can be derived as follows:

The rate of initiation is given by

$$R_i = k_i[M][SO_4^{\bullet-}] \tag{7}$$

$$R_i = \frac{d\left[SO_4^{\bullet-}\right]}{dt} = 2k_dK\left[Q^{2+}\right]_w\left[S_2O_8^{2-}\right]_w \tag{8}$$

The rate of propagation is given by

$$R_p = k_p\left[\overset{\bullet}{M}\right][M] \tag{9}$$

$$\left[\overset{\bullet}{M}\right] = \frac{R_p}{k_p[M]} \tag{10}$$

The rate of termination (R_t) is given by

$$R_t = 2k_t \left[\overset{\bullet}{M} \right]^2$$

(11)

At steady state, the rate of initiation equals to rate of termination i.e.,

$$R_i = R_t$$

(12)

$$2k_d K \left[Q^{2+} \right]_w \left[S_2O_8^{2-} \right]_w = 2k_t \left[M^{\bullet} \right]^2$$

(13)

$$\left[\overset{\bullet}{M} \right]^2 = \frac{k_d K \left[Q^{2+} \right]_w \left[S_2O_8^{2-} \right]_w}{k_t}$$

(14)

$$\left[\overset{\bullet}{M} \right] = \left[\frac{k_d K \left[Q^{2+} \right]_w \left[S_2O_8^{2-} \right]_w}{k_t} \right]^{\frac{1}{2}}$$

(15)

Using Eqs. 10 and 15, the rate of polymerization represented as follows.

$$R_p = k_p \left[\frac{k_d K}{k_t} \right]^{\frac{1}{2}} \left[Q^{2+} \right]_w^{0.5} \left[S_2O_8^{2-} \right]_w^{0.5} \left[M \right]^1$$

(16)

The above equation satisfactorily explains all the experimental observations.

5. CONCLUSION

In this present work, dual-site phase transfer catalyst has been synthesized, characterized and subjected to the study of kinetics and mechanism of the free radical polymerization of acrylonitrile.

The polymerization reactions were carried out under inert atmosphere at a constant temperature of 60^0C in ethyl acetate/water biphasic medium using $K_2S_2O_8$ as the water soluble initiators. The dependence of the rate of polymerization (Rp) on various experimental conditions such as different concentrations of [AN], [PDS], [MPTC] and temperature was discussed. From the Arrhenius plot, the energy of activation (Ea) and other thermodynamic parameters have been calculated.

Based on the kinetic results obtained, a suitable mechanism has been proposed.

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