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Phase transfer catalysed copolymerization (Kinetics and mechanism of copolymerization of acrylonitrile and styrene initiated by PDS - benzyltriphenylphosphonium chloride initiator system under biphase condition)

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ABSTRACT

The Phase–transfer radical copolymerization of acrylonitrile (AN) and styrene (ST) with benzyl-triphenylphosphoniumchloride was investigated in $K_2S_2O_8$ aqueous-organic biphase system at 65°± 0.1°C and under nitrogen atmosphere. The rate of copolymerization was expressed as the combined terms of benzyl-triphenylphosphonium ion and peroxydisulphate ion in the aqueous phase rather than the fed concentration of catalyst and $K_2S_2O_8$. The effects of varying [AN/ST], [$K_2S_2O_8$],[QX],[H^+],ionic strength of the medium, and the temperature on the rate of copolymerization (Rp) have also been studied. Rp is found to be proportional to $[AN/ST]^1$,[$K_2S_2O_8$]$^{0.5}$ and $[QX]^1$. Based on the kinetics results, a mechanism involving initiation by phase transferred $S_2O_8^{2-}$ is proposed.

Key words: Copolymerization, acrylonitrile, styrene, Phase transfer catalyst.

INTRODUCTION

Phase-transfer catalyzed reactions have received considerable attention in recent years[1]. The kinetics and mechanism of phase transfer catalysed free radical homo and copolymerization of water insoluble vinyl monomers initiated by water soluble initiators such as PMS / PDS coupled with PT-agents have received considerable attention in recent years[2,3,4]. Quaternary onium salts mixed with PMS / PDS are found to be a better initiator systems for vinyl monomers[5,6]. A wide variety of reactions such as anion displacement reactions, acrylation, alkylation, oxidation, reduction, elimination, hydrolysis, etc., could be accelerated successfully using phase-transfer catalyst. As for the applications of polymerization reactions they have been employed in condensation polymerization,(7) and anionic polymerization(8,9).

The present article describes the kinetic and mechanism of copolymerization of acrylonitrile and styrene with potassiumperoxydisulphate as initiator and benzyltriphenylphosphonium chloride as a PTC in ethylacetate/water two-phase system. Here the mixture of BTPC and PDS could act as a better radical initiator system for oil soluble monomers and if so to investigate the probable mechanism. It is in fact found that the catalytic effect of the mixture PT-agent and PDS is much greater than that of conventional free–radical initiators such as AIBN and Benozyl peroxide for oil soluble monomers[5].

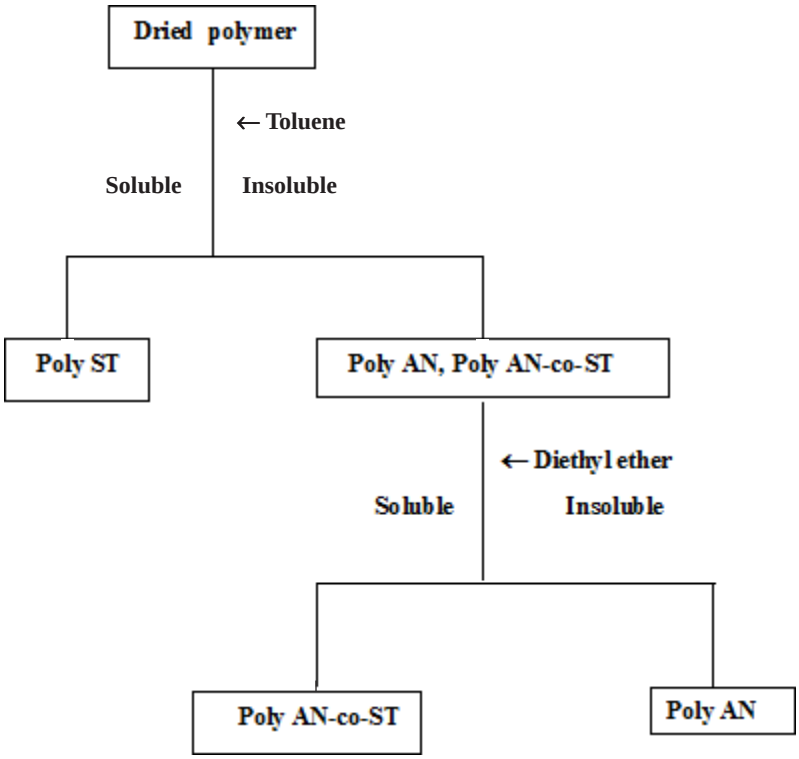
MATERIAL AND METHODS

The monomers Acrylonitrile (SD's), Styrene (Fluka) were freed from phenolic inhibitors[10] distilled and used for polymerization studies. $K_2S_2O_8$ (E.Merck) was purified by crystallization from deionized water. Benzyl-triphenylphosphonium-chloride (Fluka) was used as such without further purification. Analar grade ethylacetate was used after distillation. The other reagents used were of high purity.

Copolymerization experiments were carried out in a pyrex glass polymerization tube nitrogen atmosphere at 65°C under unstirred condition. The reaction mixture comprised 15 mL organic phase containing monomers in a required ratio and the solvent ethyl acetate and 10 mL of aqueous phase containing $K_2S_2O_8$, BTPC, H_2SO_4 and $KHSO_4$. H_2SO_4 and $K_2S_2O_8$ were used to maintain acid strength and ionic strength respectively. To make the system amenable to kinetic studies, suitable concentration of PDS, catalyst, monomer and temperature were chosen for each system. The typical copolymerization reaction involved in the following concentrations. Monomers molar ratio = 0.3 – 3.0, [PDS]= 3.0-7.0×10^{-3} mol.dm^{-3},[BTPC]=3.0– 7.0 x10^{-3} mol.dm^{-3}, μ = 1.25 mol.dm^{-3},H^+=1 mol.dm^{-3}. After conducting the experiment for given time (reaction time), the reaction mixture was poured into ice-cold methanol (containing traces of hydroquinone) to precipitate copolymers were filtered through sintered glass crucible (G.4), washed with water and methanol and dried in a vacuum hot air oven at 60°C. The dried content was assumed to be a mixture of polyacrylonitrile (Poly AN) polystyrene (Poly ST) and copolymer of acrylonitrile and styrene (PolyAN-co-ST). Dried polymer purified by reprecipitation from chloroform solution by methanol. The rate of copolymerization $Rp_{(cop)}$ were calculated from the weight of the copolymers obtained. Making use of the following equation.

$$Rp = -\frac{d[Monomers]}{dt} = \frac{1000\ W}{v\ t\ M}$$

Where, W=weight of the copolymer, v=total volume of the polymerization mixture, t=reaction time in seconds, M = molecular weight of monomers. Dried polymer purified by reprecipitation from chloroform solution by methanol. The synthesized copolymer was isolated by modified from the solubility and precipitation method has been formulated by the author and confirmed experiment. The solvents selected for isolated experiments based on the availability and on the literature reports.



Scheme 1:

RESULTS AND DISCUSSION

Steady state rate of copolymerization

Prior to the detailed kinetic study, the steady state rate of copolymerization is ascertained by determining $Rp_{(tot)}$ at different time intervals and it is found to be 150 min. (Fig.1). For detailed kinetic study, the time duration of copolymerization is fixed as 150 min. in all the experiments. Percentage conversion are also determined and presented. A plot of percentage conversion *vs* Time (Fig.2) shows that the percentage conversion increases with increasing time intervals and it is found to be level off after 150 min.

Effect of initiator concentration on Rp

The dependence of $Rp_{(tot)}$ as well as $Rp_{(cop)}$ on the concentration of initiator are examined by varying [PDS] in the range 3.0 – 7.0×10^{-3} mol.dm^{-3} at fixed monomer ratio, [BTPC], acid strength and ionic strength at 65 ± 0.1°C. $Rp_{(tot)}$ and $Rp_{(cop)}$ increases with the concentration of $K_2S_2O_8$. A plot of log$Rp_{(cop)}$ versus log [$K_2S_2O_8$] is also linear with the slope 0.5 (Fig.3) indicating the half order dependence of $Rp_{(cop)}$ on [PDS]. A plot of $Rp_{(cop)}$ versus [$K_2S_2O_8$]$^{0.5}$ is linear passing through the origin confirming the above order. A plot of $Rp_{(tot)}$ *vs* [PDS] mol.dm^{-3}.(Fig.4) gives straight line supporting the above observation. The same order with respect to initiator was also reported by *Ghosh et al*[11] in the phase transfer polymerization of styrene using $K_2S_2O_8$ as initiator at 60°C. Similar order (0.5) with respect to initiator was also reported by *Balakrishnan et al*[12] in the phase transfer polymerization of AN using $K_2S_2O_8$ as initiator at 60°C.

Effect of catalyst on Rp

At fixed concentration of PDS, monomer ratio and other parameters kept constant the effect of catalyst on Rp has been studied in the concentration range 3.0 –7.0×10^{-3} mol.dm^{-3}. It is investigated that the $Rp_{(tot)}$ and $Rp_{(cop)}$ increases with increasing concentration of catalyst (Fig.5) is a bilogarithmic plot of $Rp_{(cop)}$ versus [BTPC] is found to be linear with the slope unity indicating the order with respect to catalyst is one. Similar order with respect to catalyst was also reported by *Mandal et al*[13] in the phase transfer polymerization MMA in the presence of $K_2S_2O_8$-Bu_4NBr catalyst system in ethyl acetate / water biphase media and in the copolymerization of

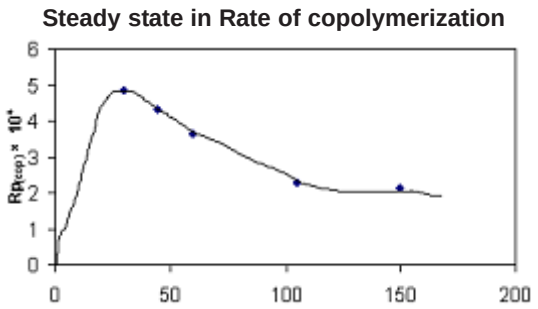


Fig. 1: Time

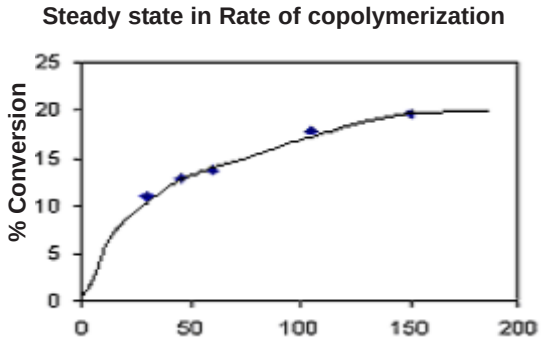
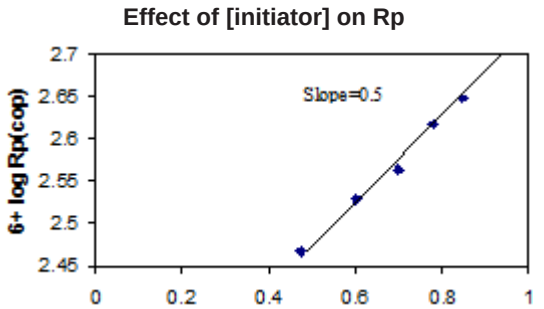


Fig. 2: Time in min



[AN/ST]= 1.0, [BTPC] =3 .0× 10^{-2} mol. dm^{-3}

[H^+] =1.0 mol. dm^{-3},μ =1.25 mol. dm^{-3}, Time =150 m

Fig. 3 + log [PDS]

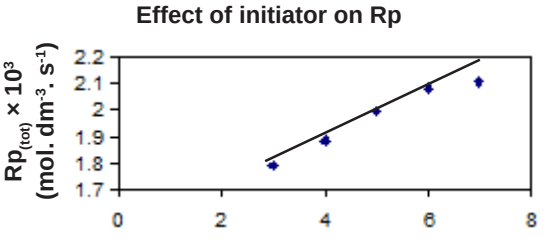


Fig. 4: [PDS] mol.dm^{-3}

acrylonitrile and methylacrylate was reported by Sang – wook and his coworkers[14].

Effect of temperature on Rp

The copolymerization experiments have been carried out at three different temperatures in the range 55 - 65°C. In all the experiment, the concentration of the monomer ratio, PDS and PT-agent, ionic strength, etc., are kept constant. The rate of copolymerization of the monomers are found to be increased with an increasing temperature. The over all activation energy of copolymerization (Ea) obtained from the plot of $\log Rp_{(cop)}$ vs $1/T \times 10^{-3}$ (deg^{-1}) is 9.152 k.cal. mol^{-1} (Fig:7) for the systems AN and ST with BTPC.

Effect of (v_o/v_w) on Rp

Since the formation or transfer of free-radical aqueous to organic phase is responsible for the copolymerization, volume ratio has some effect on the $Rp_{(cop)}$ in biphase condition. At fixed concentration of monomer ratio, initiator, catalyst and the other parameters are kept constant, the experiments are performed at different volume ratio by changing the volume of organic phase and

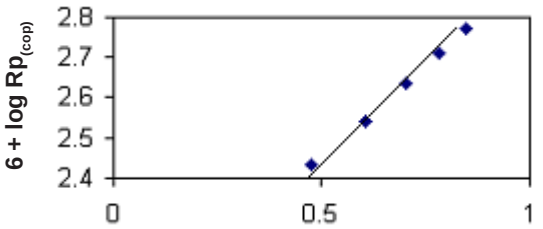


Fig. 5: -3 + log [BTPC]

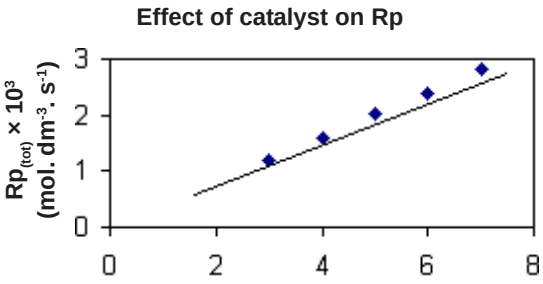
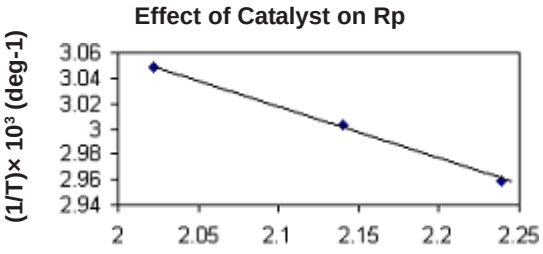
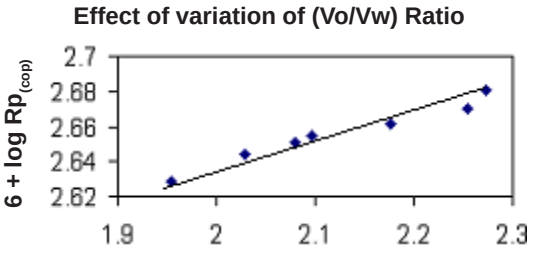


Fig. 6: [BTPC] mol.dm^{-3}



[AN/ST]= 1.0, [PDS] = 3.0 × 10^{-2} mol. dm^{-3}, [H^+] =1.0 mol. dm^{-3}, μ =1.25 mol. dm^{-3},Time =150 min

Fig. 7: 6+ log $Rp_{(cop)}$



[AN/ST]= 1.0, [PDS] = 3.0 × 10^{-2} mol. dm^{-3}, [BTPC] =3 .0× 10^{-2} mol. dm^{-3} [H^+] =1.0 mol. dm^{-3}, μ =1.25 mol. dm^{-3}, Time =150 min.

Fig. 8: -2 +log (Vo/Vw)

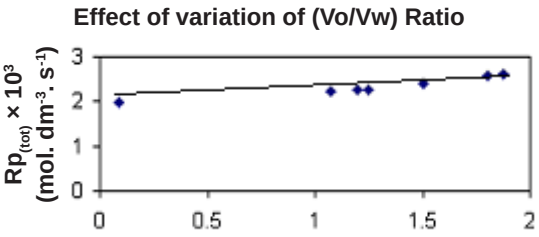
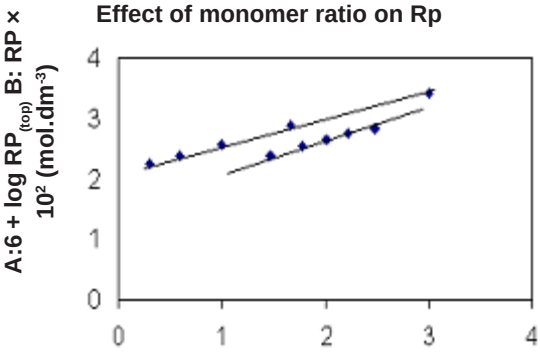


Fig. 9: (Vo/Vw) ratio



A:2 + log [AN/ST] B: [AN/ST

Fig.9: - [PDS] = 3 × 10^{-2} mol. dm^{-3}, [BTPC] = 3 × 10^{-2} mol. dm^{-3}, [H^+] = 1.0 mol. dm^{-3} μ = 1.25 mol.dm^{-3} Temperature = 65 ± 0.1° C

aqueous phase respectively (Fig.8). It shows that the copolymerization rate decreases with decreasing volume ratio *ie.* increases with increasing volume of organic phase or decreases with increasing aqueous phase. Similar observation have also reported by *Ghosh et a1*[15]

Effect of monomer ratio on Rp

The effect of monomers ratio on $Rp_{(cop)}$ and $Rp_{(tot)}$ are studied by varying concentration of acrylonitrile and styrene in the monomer ratio range 0.3 to 3 at fixed concentration of initiator (0.02 $mol.dm^{-3}$) BTPC (0.02 $mol.dm^{-3}$), acid strength (1.0 mol. dm^{-3}) and ionic strength (1.25 mol. dm^{-3}). Rp increases with the concentration ratio of the monomers. A plot of $Rp_{(cop)}$ versus log [monomer ratio] is linear with a slope 1.0 indicating the dependence of Rp on $[M_1/M_2]$ is first order (Fig.9 A). It is also verified by a plot of $Rp_{(tot)}$ versus [monomer ratio] which is linear (Fig.9 B). Similar observation are also recorded on the total rate of polymerization with the monomer ratio. Similar kinetics behaviour have also reported by park et al[14] in study of phase transfer copolymerization of AN and MA.

Mechanism and rate law

Based on the kinetic results observed in the copolymerization of acrylonitrile, styrene monomers initiated by PDS – BTPC initiator system in Ethyl acetate/water biphase condition and considering the reaction steps mentioned in the Fig. 1

Fig.1 presents the reactions characterizing the copolymerization of AN (M_1) ST(M_2) initiated by $K_2S_2O_8$ – BTPC in ethyl acetate / water biphase

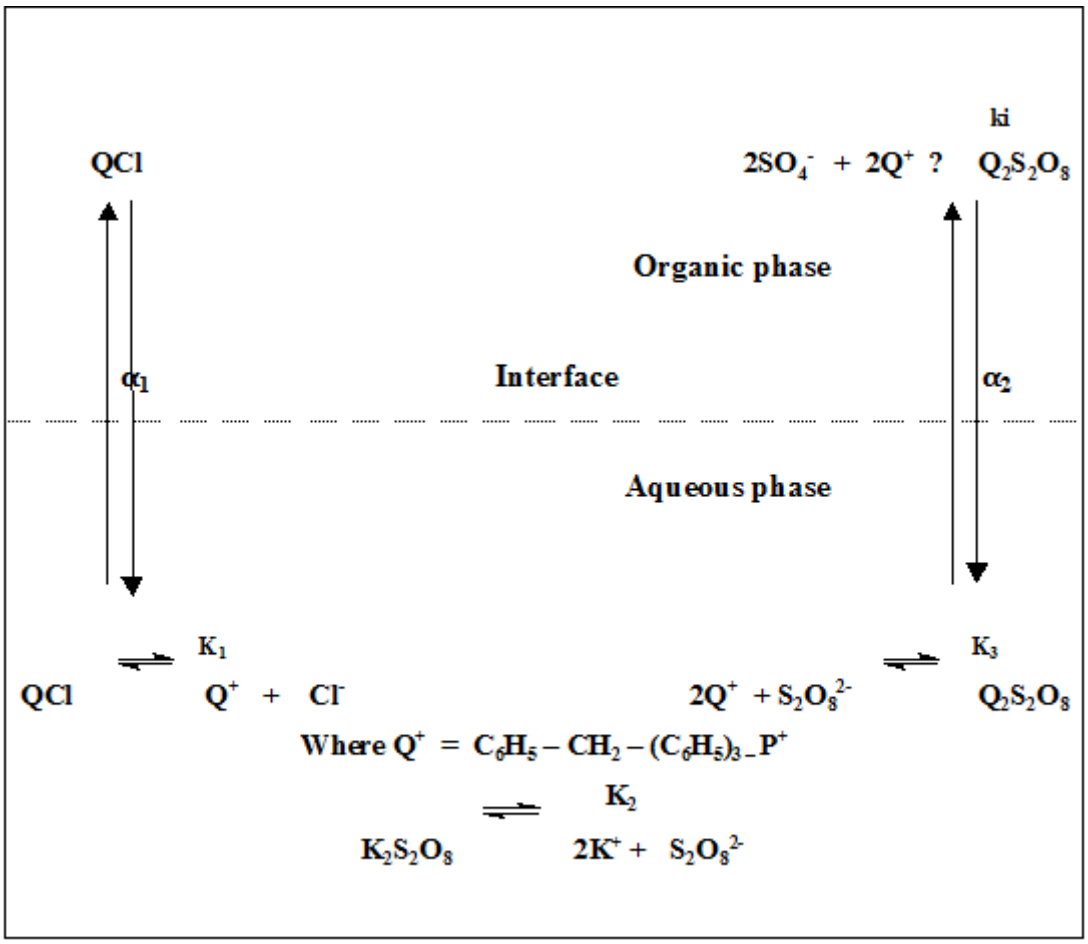


Fig. 1: Copolymerization pathways with PDS-PT agent in an aqueous organic biphase system

systems. It is assumed that dissociation of QCl and $K_2S_2O_8$, formation of $Q_2S_2O_8$ complex in aqueous phase, distribution of $Q_2S_2O_8$ transferred into organic phase and decomposition of PDS – Q^+ - complex into the active $SO_4^{\cdot-}$ radicals by the interaction of the solvent / monomers to initiate polymerization. The following mechanism have been proposed for the copolymerization of acrylonitrile styrene under phase transfer condition.

Mechanism

Aqueous phase

PDS & PT- agents equilibrium steps

$$QCl \underset{}{\overset{K_1}{\rightleftharpoons}} Q^+ + Cl^- \qquad ...(1)$$
$$K_2S_2O_8 \overset{K_2}{\rightleftharpoons} 2K^+ + S_2O_8^{2-}$$

Interface

$$2[Q^+](w) + [S_2O_8^{2-}](w) \rightleftharpoons [Q^+]_2S_2O_8^{2-}(w) \longrightarrow [Q_2S_2O_8^{2-}]_{(o)} \qquad ...(2)$$

(PDS-Q^+ complex)

Organic Phase

$$Q_2S_2O_8 \xrightarrow{K_i} 2Q^+ + 2SO_4^{\cdot-} + M \rightarrow SO_4\text{-}M \qquad ...(3)$$

where $M=M_1/M_2$

Propagation

$$M_1SO_4^{\cdot} + M_1 \xrightarrow{k_{p11}} SO_4M_1M_1$$
$$M_1SO_4^{\cdot} + M_2 \xrightarrow{k_{p12}} SO_4M_1M_2$$
$$M_2SO_4^{\cdot} + M_1 \xrightarrow{k_{p21}} SO_4M_2M_1$$
$$M_2SO_4^{\cdot} + M_2 \xrightarrow{k_{p22}} SO_4M_2M_2 \qquad ...(4)$$

Termination

$$\sim M_1 + \sim M_1 \xrightarrow{k_{t1}} \text{Polymer (homo type)}$$
$$\sim M_1 + \sim M_2 \xrightarrow{k_{t12}} \text{Polymer (hetero type)}$$
$$\sim M_2 + \sim M_1 \xrightarrow{k_{t21}} \text{Polymer (hetero type)} \qquad ...(5)$$
$$\sim M_2 + \sim M_2 \xrightarrow{k_{t2}} \text{Polymer (homo type)}$$

Derivation of Rate law

The equilibrium constants K_1, K_2, K_3 in the reactions and distribution constants α_1 , α_2 of QCl and $Q_2S_2O_8$ are defined as follows; respectively,

$$K_1 = \frac{[Q^+]_{(w)}[Cl^-]_{(w)}}{[Q^+Cl]_{(w)}} \qquad ...(6)$$

$$K_2 = \frac{[K^+]^2_{(w)}[S_2O_8^{2-}]_{(w)}}{[K_2S_2O_8]_{(w)}} \qquad ...(7)$$

$$K_3 = \frac{[Q_2S_2O_8]_{(w)}}{[Q^+]^2_{(w)}[S_2O_8^{2-}]_{(w)}} \qquad ...(8)$$

$$\alpha_1 = \frac{[Q^+Cl^-]_{(w)}}{[QCl]_{(O)}} \qquad ...(9)$$

$$\alpha_2 = \frac{[Q^+S_2O_8^{2-}]_{(w)}}{[Q_2S_2O_8]_{(o)}} \qquad ...(10)$$

The rate law for the copolymerization based on this mechanism can be derived as follows:

The rate of initiation is

$$R_i = 2fk_i[Q_2S_2O_8] \qquad ... (11)$$

f = efficiency of initiator

Considering the equation (8),

$$[Q_2S_2O_8] = K_3[Q^+]^2_{(w)}[S_2O_8^{2-}]_{(w)} \qquad ...(12)$$

substituting eqn (12) in eqn (11), we get

$$Ri = 2ki f K_3[Q^+]^2_{(w)}[S_2O_8^{2-}]_{(w)} \qquad ...(13)$$

The rate of propagation steps (eqn.4) in the reaction are

$$Rp^1 = d[M_1]/dt = k_{11}[M_1][M_1] + k_{21}[M_2][M_1] \quad ...(14)$$
$$Rp^2 = d[M_2]/dt = k_{22}[M_2][M_2] + k_{12}[M_1][M_2] \quad ...(15)$$

In general, termination of the polymer is dependent on the forms of radicals. The termination step in the copolymerization constitutes three kinds of termination (eqn-5) and the rate of termination is expressed as follows.

$$R_t = 2k_{t1}[M_1]^2 + 2k_{t12}[M_1][M_2] + 2k_{t2}[M_2]^2 \qquad ...(16)$$

The rate of termination of AN is written as eqn.(17) because the second and third term of eqn.(16) may be neglected in the termination of AN with coupling, and the rate of termination of ST is written as eqn.(18) because the first and second

term may be neglected in the termination of ST with disproportionation.

$$R_{t1} = 2k_{t1}[M_1]^2 \quad ...(17)$$
$$R_{t2} = 2k_{t2}[M_2]^2 \quad ...(18)$$

Using eqn.(13), (17) and (18) at steady state, the initial rate of polymerization of eqn.(14) and (15) may be written as

$$R_i = R_{t1}, \quad R_i = R_{t2}$$

$$R_i = 2k_i f K_3 [Q^+]^2_{(w)} [S_2O_8^{2-}]_{(w)}$$
$$R_{t1} = 2k_{t1}[M_1]^2, \; r_{t2} = 2k_{t2}[M_2]^2$$

$$[M_1] = \frac{2K_1 f k_3}{2k_{t1}} [Q^+]_{(w)} [S_2O_8^{2-}]^{1/2}_{(w)} \quad ...(19)$$

$$[M_2] = \frac{2K_1 f k_3}{2k_{t2}} [Q^+]_{(w)} [S_2O_8^{2-}]^{1/2}_{(w)} \quad ...(20)$$

Substituting $[M_1]$ and $[M_2]$ from eqn (19) and (20) respectively in to the eqn (14) and (15) accordingly, Where $[M_1]_\circ$ and $[M_2]_\circ$ are the feed concentration of monomer M_1 and M_2 respectively.

$$Rp^1 = \left[\left(\frac{k^2_{11}}{2k_{t1}}\right)^{1/4} + \left(\frac{k^2_{21}}{2k_{t2}}\right)^{1/4}\right]\left(\frac{2fk_1k_3}{\alpha_2}\right)^{1/4} [Q^+]_{(w)}[S_2O_8^{2-}]^{1/4}[M_1]_\circ \quad ...(21)$$

$$Rp^2 = \left[\left(\frac{k^2_{22}}{2k_{t2}}\right)^{1/2} + \left(\frac{k^2_{12}}{2k_{t1}}\right)^{1/2}\right]\left(\frac{2fk_1k_3}{\alpha_2}\right)^{1/2} [Q^+]_{(w)}[S_2O_8^{2-}]^{1/2}[M_2]_\circ \quad ...(22)$$

Adding eqn.(21) to (22) and taking concentration of Q^+ as total concentration by mass balance of species, Q the total initial rate of polymerization may be written as

$$R_{pt} = C(B_1 f_1 + B_2) \quad ...(23)$$
$$\text{Where, } f_1 = [M_1]_\circ / [M_2] \quad ...(24)$$

$$B_1 = \left[\left(\frac{k^2_{11}}{2k_{t1}}\right)^{1/4} + \left(\frac{k^2_{21}}{2k_{t2}}\right)^{1/4}\right]\left(\frac{2fk_1k_3}{\alpha_2}\right)^{1/4} [M_2]_\circ \quad ...(25)$$

$$B_2 = \left[\left(\frac{k^2_{22}}{2k_{t2}}\right)^{1/4} + \left(\frac{k^2_{12}}{2k_{t1}}\right)^{1/4}\right]\left(\frac{2fk_1k_3}{\alpha_2}\right)^{1/4} [M_2]_\circ \quad ...(26)$$

$$C = \frac{[Q^+]^T_{(w)}[S_2O_8^{2-}]^{1/4}_{(w)}}{1 + \frac{[Q^+]_{(w)}}{2} K_3 [Q^+]_{(w)}[S_2O_8^{2-}]_{(w)}} \quad ...(27)$$

Here, $[Q^+]^T_w = [Q^+]_w + [QCl]_w + [Q_2S_2O_8]_w$ ...(28)

Using the reaction in eqn.(13), the rate of copolymerization containing only cross – propagation of AN and ST at steady state may be written as

$$R_{pco} = k_{21}[M_2][M_1] + k_{12}[M_1][M_2] \quad ...(29)$$

The rate of copolymerization of AN and ST may be derived as eqn. (29) by using the procedures as similar to those for derivation of the total rate of polymerization.

$$R_{pco} = C(B_3 f_1 + B_4) \quad ...(30)$$

$$B_3 = \left(\frac{K^2_{21}}{2K_{t2}}\right)^{1/4}\left(\frac{2fk_1k_3}{\alpha_2}\right)^{1/4} [M_2]_\circ \quad ...(31)$$

$$B_4 = \left(\frac{K^2_{12}}{2K_{t1}}\right)^{1/4}\left(\frac{2fk_1k_3}{\alpha_2}\right)^{1/4} [M_2]_\circ \quad ...(32)$$

The above rate law derived are formed to be consist with the experimental results *i.e.,* the orders with respect to initiator, catalyst, and monomer ratio are 0.5, 1.0, 1.0 respectively.

Abbreviations and symbols

PTC	-	Phase Transfer Catalysis
PT-agent	-	Phase Transfer Agent
AN	-	Acrylonitrile
ST	-	Styrene
AIBN	-	Azobisisobutyronitrile
PMS	-	Peroxomonosulphate
PDS	-	Peroxydisulphate
QX	-	Quaternary ammonium salt
BTPC	-	Benzyltriphenylphosphonium chloride
(O)	-	Organic phase
(W)	-	Aqueous phase
$[H^+]$	-	Acid strength
μ	-	Ionic strength
TºC	-	Temperature in centigrade
TK	-	Temperature in Kelvin
$Rp_{(tot)}$	-	Rate of total polymerization
$Rp_{(cop)}$	-	Rate of copolymerization
E_a	-	Energy of activation
k_i	-	Rate constant for chain

		initiation			termination
k_p	-	Rate constant for chain propagation	K_1,K_2,K_3	-	Equilibrium constants
			$\pm_1,\pm_2$	-	Distribution constants
k_t	-	Rate constant for chain			

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