

Role of Phase Transfer Catalyst in Radical Polymerization of Butyl Acrylate Using Peroxomonosulphate and Disulphate as Water Soluble Initiators – A Comparative Kinetic Study

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This work describes the experimental kinetic investigation involving free radical solution polymerization of butyl acrylate initiated by water soluble peroxomono and disulphate. Polymerization was accomplished without stirring at 60 °C in absence of oxygen in cyclohexanone/water biphse media. The experiments were conducted at various concentrations of monomer, catalyst, initiator and various temperatures. A suitable mechanism has been propounded based on the radical polymerization.

Key Words: Phase transfer catalyst, Free radical polymerization, Kinetics, Mechanism.

INTRODUCTION

Lack of homogeneity of the reaction mixture is an vital factor which contributes slowness or non-feasibility of chemical reactions. This problem can be eradicated by the use of phase transfer catalyst. A number of chemicals are produced commercially by using phase transfer catalyst¹⁻⁴. This technology is also used in preventing and controlling pollution and used in eliminating destructive impurities in waste and product streams. Apart from this it provides compelling benefits such as faster reaction rate, obtain higher conversions or yields, make fewer by products, eliminate the need for expensive or dangerous solvents that will dissolve all the reactants in one phase, eliminate the need for expensive raw materials and/or minimize waste problems. Phase transfer catalysts are especially useful in green chemistry- by allowing the use of water, the need for organic solvents is reduced. The technology of phase transfer catalyst has been successfully exploited and a great number of papers are available in the literature⁵⁻¹⁶. The aim of this article is to study the influence of phase transfer catalyst in the free radical and to produce a polymer with good mechanical, optical properties, which will be a potential material for demanding applications.

EXPERIMENTAL

Butyl acrylate (SRL, Mumbai), 1-bromo hexane (SRL Chemicals, Mumbai), tetramethyl ethylenediamine (SRL Chemicals, Mumbai), potassium peroxomonosulfate (Sigma Aldrich, Germany), potassium peroxodisulfate (Merck, India) were used as such. Solvents such as ethanol, cyclohexanone (Thomas Baker, Chennai) were purchased and are purified by distillation and used. Phase transfer catalyst 1,4-*bis*-(dimethylhexyl)ethylenediammonium bromide has been synthesized in the laboratory. Double-distilled water was used throughout the experiment for the preparation of reagents and solutions.

Synthesis of phase transfer catalyst : Measured quantity of one equivalent of tetramethylethylenediamine (0.01 mol) and two equivalent of 1-bromo hexane (0.02 mol) was introduced into a 250 mL flask and were refluxed at 60 °C in an oil bath along with vigorous stirring for 6 h. The crude sample obtained was recrystallized from ethanol to get 1,4-*bis*-(dimethylhexyl) ethylene diammonium bromide (**Scheme-I**).



Characterization of phase transfer catalyst: Phase transfer catalyst has been subjected to FT-IR to confirm the functional groups present in it and proton and ¹³C NMR are

used to find out the protons and the back bone of the synthesized compound^{12,13}.

FT-IR: Peaks present in 3014 cm⁻¹ and 2962 cm⁻¹ are assigned for asymmetric and symmetric stretching for C-H and the peak at 1495 cm⁻¹ denotes the methylene group bending and also 1120 cm¹ is confirming the presence of saturated C-N linkage. Out-of-plane bending of C-H is shown in the peak at 949 cm⁻¹(Fig. 1).



Proton NMR: The signal at δ 4.6 appeared as quartet which implies the -CH₂ protons from amine part of the catalyst and at δ 3.30 shows a singlet confirms the -CH₃. The proton attached to electron donating group (N-CH₂) gives a quartet at δ 3.24. The -CH₂ protons produced a signal at δ 1.73 to δ 1.33 for the alkyl halide and terminal methyl proton appears as triplet at δ 1.1 (Fig. 2).



¹³**C NMR:** Signal at δ 62.04 (N-C) shows that carbon attached to the amine group and δ 61.57 confirms the bridging carbon (-N-CH₂-N-CH₂) present in the amine. The signal present around δ 55 corresponding to the -CH₃ carbons attached to the amine and the signal around δ 53 corresponds to the -CH₂ carbon atom and finally the terminal methyl carbon atom shows signal δ 16.27 (Fig. 3).



CHN analysis: Synthesized phase transfer catalyst has been subjected to elemental analysis, the results shows that for carbon 45.11, nitrogen 7.87, hydrogen 8.02 and for bromine 34.22.

Polymerization technique: The polymerizations were conducted in closed pyrex glass vials under oxygen free atmosphere. The monomer in cyclohexanone forms the organic phase and the aqueous phase comprises of phase transfer catalyst, sodium bisulphate and sulphuric acid in water. This reaction mixture was engrossed into the thermostat maintained at constant temperature, purged with nitrogen for 0.5 h and then the glass vials are sealed to maintain inert atmosphere. The polymerization reactions are made alive by adding a calculated quantity on initiator and stop watch started simultaneously. The precipitate was formed continuously during the polymerization and the reaction was quenched by pouring the reaction mixture into ice-cold methanol containing traces of hydroquinone. The polymer was isolated through a G-4 sintered crucible and washed with double distilled water, methanol and dried in a vacuum oven to constant weight.

Rate of polymerization was evaluated by gravimetry using the following equation:

Rate of polymerization =
$$\frac{1000 \times W}{V \times t \times M}$$

where, W = weight of the polymer in gram, M = molecular weight of the monomer, V = volume of the reaction mixture, t = reaction time in seconds.

RESULTS AND DISCUSSION

Steady state approximation: The influence of reaction time on the rate of polymerization (Rp) was evaluated by varying the time. The time taken to attain the steady state rate of polymerization to carry out the further experiments was found to be 40 min for both the per oxo monosulphate (PMS) and disulphate (PDS) initiators. An increase in the rate of polymerization was observed initially which then decreased and then remained constant (Fig. 4).

Influence of [monomer] on rate of polymerization: The samples were prepared using different amounts of monomer, while the concentration of initiator and phase transfer catalyst are fixed constant at 60 °C. For this two type of initiators, the rate of polymerization has been increased with increasing concentration monomer (Figs. 5 and 6) and the order of reactivity delivers same (*i.e.*) unity.



Influence of [initiator] on rate of polymerization: At a monomer concentration of 2 mol dm⁻³, phase transfer catalyst concentration of 0.02 mol dm⁻³ and constant ionic strength of 0.05 M, the effect of per oxo monosulphate (PDS) and per

oxo disulphate (PMS) concentrations on Rp was studied by varying the concentration range 0.015-0.025 mol dm⁻³. The order with respect to the PMS and PDS were found to be unity. The plot of Rp *vs.* log [PDS] and Rp *vs.* log [PDS] were found to be linear and it confirms by passing through the origin (Figs. 7 and 8). Increasing the concentration of initiator influences the number of initiating radical which accelerates the free radical polymerization reaction.



Influence of [PTC] on rate of polymerization: At a fixed concentration of monomer, peroxo disulphate and peroxo monosulphate and constant ionic strength of 0.05 M, the effect of phase transfer catalyst concentration on Rp was studied from the range of 0.0075-0.0125 mol dm⁻³. The plot of log Rp *vs.* log [PTC] for mono and di sulphate initiators were found to be linear and the order was found to be one (Figs. 9 and 10). Phase transfer catalyst plays a major role in this reaction, increasing it's concentration by catalytic amount the reaction is favoured in the forward direction. Increase in the concentration of catalyst favours the formation of number of ion-pairs, which increases the rate of polymerization.



Effect of temperature on rate of polymerization: The effect of temperature on rate of polymerization is presented in Fig.11 for Arrhenius plot and Fig.12 denotes for Eyring plot. The rate of polymerization increased dramatically with the increase in temperature and according to these results, the thermodynamic parameters were evaluated (Table-1).





TABLE-1 THERMODYNAMIC PARAMETERS				
Systems	Ea (kJ/mol)	$\frac{\Delta S}{(J \text{ K}^{-1} \text{mol}^{-1})}$	ΔH (kJ/mol)	∆G kJ/mol)
KHSO ₅ -PTC system	13.96	-89.42	11.88	41.16
$\mathbf{K}_2\mathbf{S}_2\mathbf{O}_8$ -PTC system	91.55	140.75	89.30	42.04

Kinetic scheme and mechanism

i) KHSO5-PTC system (a) Phase transfer

(c) Initiation

$$\begin{array}{ccc} \mathbf{Q}^{+}\mathbf{SO}_{4}^{-} + \mathbf{M} & \xrightarrow{\mathbf{k}_{1}} & \mathbf{M}_{1}^{-}(\mathbf{M}^{-}\mathbf{O}^{-}\mathbf{SO}_{3}^{-}\mathbf{Q}^{+}) \\ (\mathbf{0}) & (\mathbf{0}) & (\mathbf{0}) \end{array}$$

(d) Propagation

$$M_1 + M \xrightarrow{k_p} M_2$$
$$M_{n-1} + M \xrightarrow{k_p} M_n$$

(e) Termination

$$2M'_n \xrightarrow{k_t} polymen$$

ii) K₂S₂O₈-PTC system

- (a) Phase transfer $(Q^+)S_2O_8^{-2-}$ 20^{+} S208 (0) (w) (w)
- (b) Decomposition

$$(Q^+)_2 S_2 O_8^{2} \xrightarrow{\kappa_d} 2Q^+ SO_4^{*}$$
(0)
(0)

(c) Initiation $M_1(M-O-SO_3Q^+)$ $Q^+SO_4^- + M$ (0) (0) (d) Propagation

$$M_1 + M \xrightarrow{k_p} M_2$$

$$M_1 + M \xrightarrow{k_p} M_2$$

'n

(e) Termination

$2M_n \xrightarrow{k_t} polymer$

This mechanism involves the formation of quaternary ammoniumperoxy monosulfate complex $Q^+HSO_5^-/quaternary$ ammoniumperoxydisulfate complex $(Q^+)_2S_2O_8^{2-}$ in the aqueous phase, which is then transferred to the organic phase. The decomposition of this ion-pair takes place in the organic phase, leading to the formation of $Q^+SO_4^-$. Applying the general principles of free-radical polymerization and stationary-state hypothesis to the radical species, the rate law for this mechanism can be written as:

$$R_{p} = k_{p} \left(\frac{k_{d}K}{k_{t}}\right) \frac{[M][HSO_{5}^{-}][Q^{+}]_{Total}}{1 + k[Q^{+}]_{w}[HSO_{5}^{-}]_{w}}$$
$$R_{p} = k_{p} \left(\frac{k_{d}K}{k_{t}}\right) \frac{[M][S_{2}O_{8}^{2-}]^{1.5}[Q^{+}]_{Total}^{0.5}}{1 + k[Q^{+}]_{w}[S_{2}O_{8}^{2-}]_{w}}$$

This expression satisfactorily explains all the experimental results and observations. The above expression for rate of polymerization explains the experimental observations satisfactorily.

Conclusion

The active di-sited phase transfer catalyst has been synthesized and characterized by FT-IR, NMR and the elements present in the catalyst have been analyzed by CHN analysis. The polymerization of butylacrylate under phase transfer conditions denotes the efficiency of the peroxomonosulphate over peroxodisulphate as initiators. The polymerization rate is dependent on the parameters such as concentrations of monomer, catalyst and the effect of temperature. According to mono and disulphate initiators the above parameters have been studied kinetically, which shows the rate of polymerization and the order of reaction are better for the peroxomonosulphate than the disulphate, this might be due to the rate of mobility of the radicals. While accounting for the Arrhenius parameter monosulphate radicals having less activation energy comparing to the other one, more over other thermodynamic parameters such as enthalpy, entropy, free energy also clearly evidences for the better rate of reaction. Depends upon the kinetic values a suitable mechanism's have been proposed.

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