

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 cm⁻¹ 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).

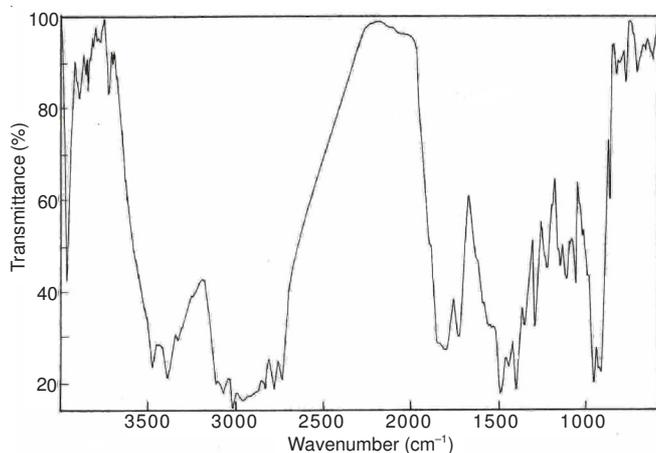


Fig. 1. FT-IR of phase transfer catalyst

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).

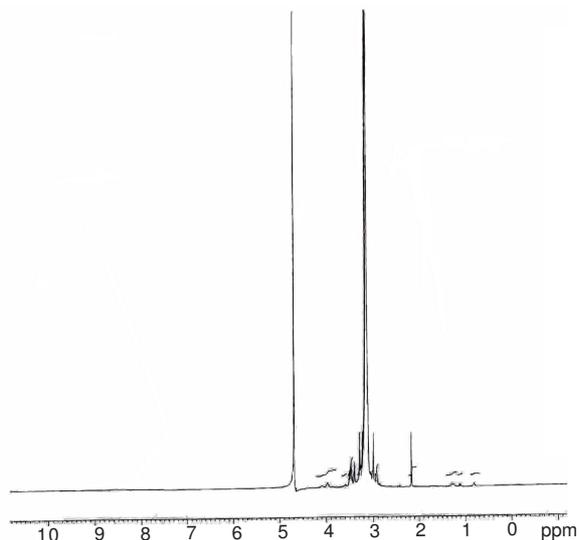


Fig. 2. ¹H NMR of phase transfer catalyst

¹³C 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).

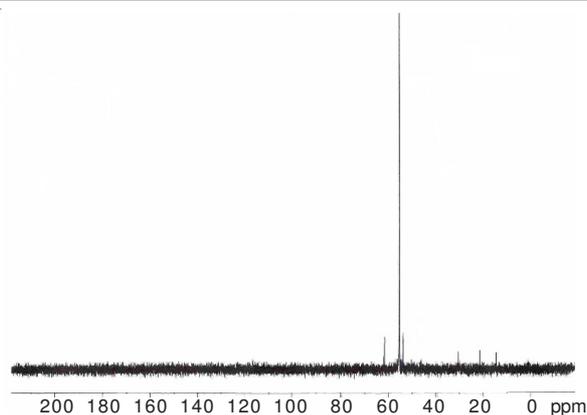


Fig. 3. ¹³C NMR of phase transfer catalyst

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:

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

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 (R_p) 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.

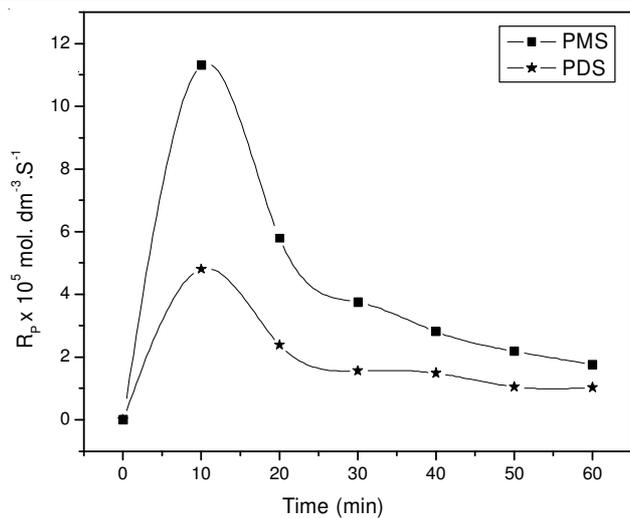


Fig. 4. Steady state approximation

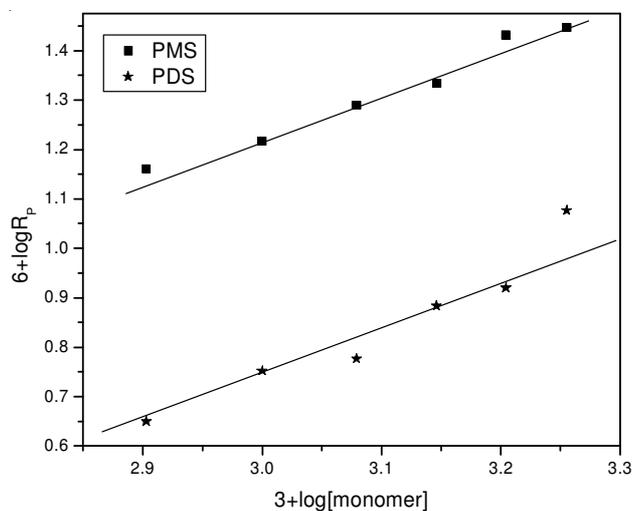


Fig. 5. Effect of monomer concentration on rate of polymerization

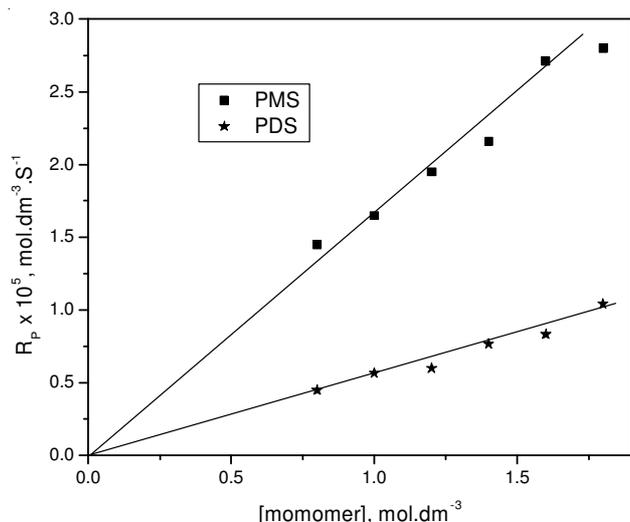


Fig. 6. Conformation plot

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 R_p was studied by varying the concentration range $0.015\text{-}0.025 \text{ mol dm}^{-3}$. The order with respect to the PMS and PDS were found to be unity. The plot of R_p vs. $\log [\text{PDS}]$ and R_p vs. $\log [\text{PMS}]$ 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.

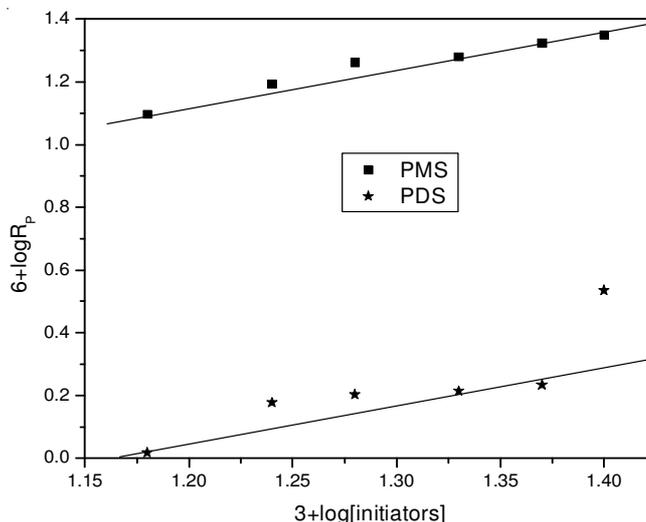


Fig.7. Effect of initiator Variation

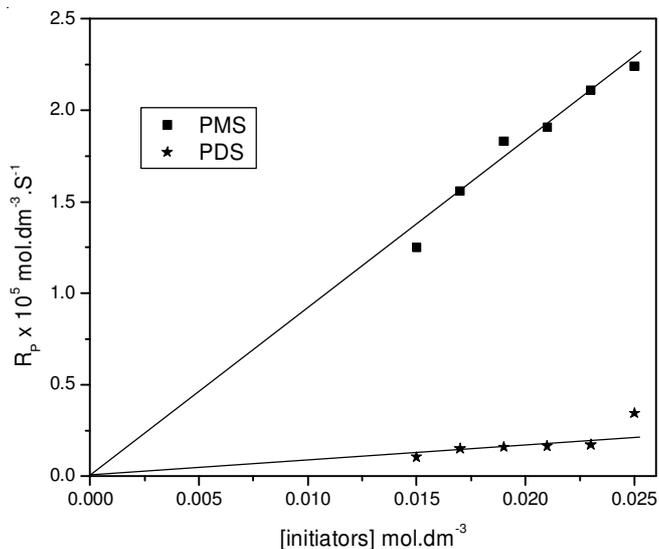


Fig. 8. Conformation plot

Influence of [PTC] on rate of polymerization: At a fixed concentration of monomer, peroxy disulphate and peroxy monosulphate and constant ionic strength of 0.05 M , the effect of phase transfer catalyst concentration on R_p was studied from the range of $0.0075\text{-}0.0125 \text{ mol dm}^{-3}$. The plot of $\log R_p$ vs. $\log [\text{PTC}]$ 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 its 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.

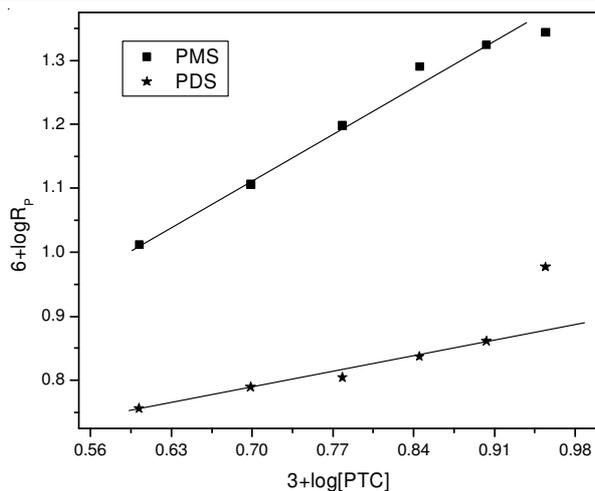


Fig.9. Effect of catalyst Variation

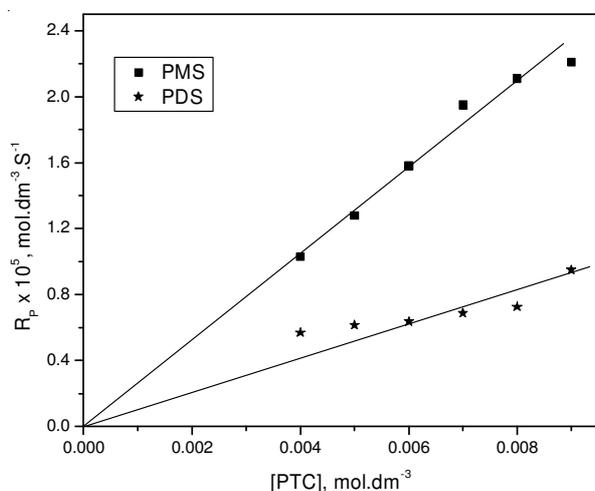


Fig. 10. Conformation plot

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).

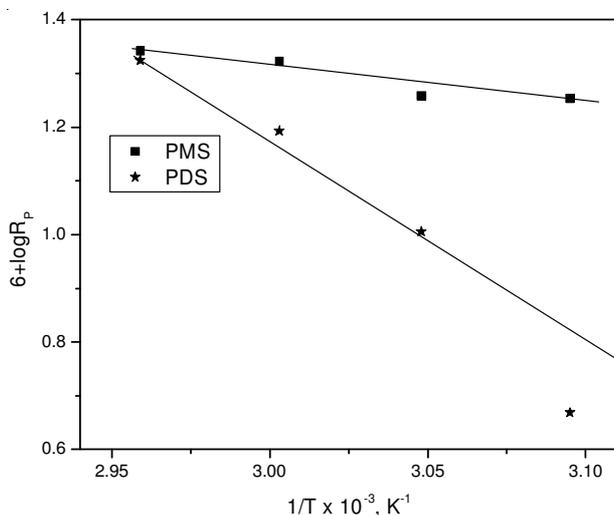


Fig.11. Arrhenius plot

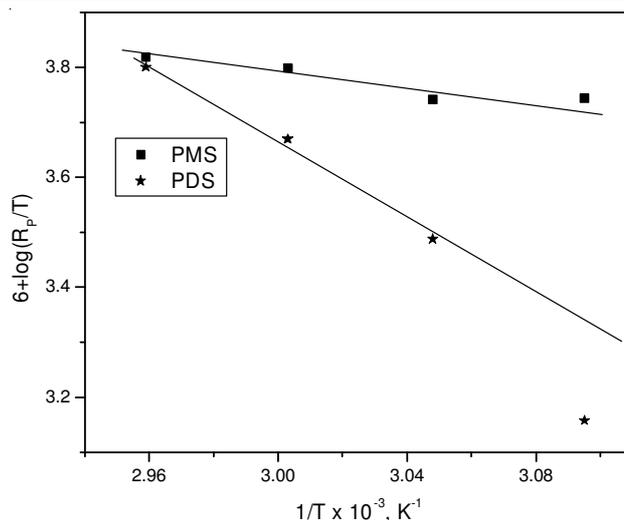


Fig.12. Eyring plot

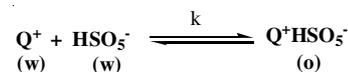
TABLE-1
THERMODYNAMIC PARAMETERS

Systems	Ea (kJ/mol)	ΔS (J K ⁻¹ mol ⁻¹)	ΔH (kJ/mol)	ΔG (kJ/mol)
KHSO ₅ -PTC system	13.96	-89.42	11.88	41.16
K ₂ S ₂ O ₈ -PTC system	91.35	140.73	89.50	42.64

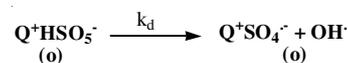
Kinetic scheme and mechanism

i) KHSO₅-PTC system

(a) Phase transfer



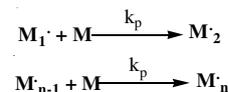
(b) Decomposition



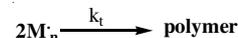
(c) Initiation



(d) Propagation

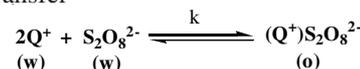


(e) Termination

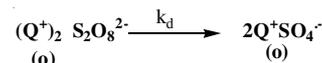


ii) K₂S₂O₈-PTC system

(a) Phase transfer



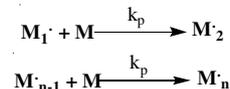
(b) Decomposition



(c) Initiation



(d) Propagation



(e) Termination



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:

$$R_p = k_p \left(\frac{k_d K}{k_t} \right) \frac{[M][HSO_5^-][Q^+]_{\text{Total}}}{1 + k[Q^+]_w [HSO_5^-]_w}$$

$$R_p = k_p \left(\frac{k_d K}{k_t} \right) \frac{[M][S_2O_8^{2-}]^{1.5}[Q^+]_{\text{Total}}^{0.5}}{1 + k[Q^+]_w [S_2O_8^{2-}]_w}$$

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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