CHAPTER 4

SUMMARY AND CONCLUSION

In the present study two new phase transfer catalysts - a single site phase transfer catalyst and a di-site phase transfer catalyst have been synthesized, characterized and employed for the free radical polymerization of four different alkyl methacrylates namely, methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA) and glycidyl methacrylate (GMA). The polymerization reactions were carried out in water/ethyl acetate biphasic media using water soluble potassium peroxydisulphate initiator under unstimulated condition in the inert atmosphere at 60 ± 1°C. Kinetic study of polymerization reactions has been done by varying the concentration of monomer, initiator, PTC and varying the volume fraction of aqueous phase, ionic strength, acid strength and the temperature. Molecular weights of synthesized polymers were determined by gel permeation chromatographic technique. The efficiency of catalysts has been checked by comparing the rate of polymerization and molecular weight of polymers.

The synthesized single site phase transfer catalyst, 2-benzoylethyl decyldimethylammonium bromide [BEDDAB] and the di-site phase transfer catalyst, 1,1,4,4-tetramethyl-1,4-dioctyl ethylene diammonium bromide [TDEDB] have been confirmed by FT-IR, $^1$H-NMR and $^{13}$C-NMR. The elemental analysis data for the synthesized catalysts are found to be in agreement with the theoretical values.
The phase transfer catalyst aided free radical polymerization reactions of four different alkyl methacrylate monomers were carried out under identical conditions using both the catalysts. The following observations have been made during polymerization of all the monomers using BEDDAB and TDEDB as phase transfer catalysts in ethyl acetate/water biphasic media.

i. The polymerization reactions proceeded with measurable rates and it was not affected by stray light indicating that there was no photochemical initiation.

ii. The oxidation of monomer by PDS was not observed under deaerated conditions.

iii. The polymerization reactions were found to be retarded by the presence of air or oxygen and hydroquinone indicating the free radical polymerization.

iv. The rate of polymerization was not changed appreciably by variation in pH and ionic strength.

v. Change of cation from K$^+$ to NH$_4^+$ in PDS made no difference in the rate of polymerization indicating the transfer of the anion S$_2$O$_8^{2-}$ from the aqueous phase to the organic phase depends only on the organic nature of the catalyst cation.

vi. Variations in the hydrogen ion concentration and ionic strength of aqueous phase are not found to change the Rp appreciably.

vii. The systems remained clear during polymerization of the monomers (MMA, EMA, BMA and GMA).
The steady state rates of polymerization for the four monomers viz., MMA, EMA, BMA and GMA were found out by determining the Rp at different intervals of time. A plot of Rp versus time shows an increase initially and then slight decrease thereafter and then remains constant. The steady state rates of polymerization of the all the four monomers were obtained within 30-50 minutes when BEDDAB was used. The polymerization reactions were carried out at 60 ± 1°C with the reaction time of 40 minutes for all the four monomers. The steady state rates of polymerization were obtained as 50, 50, 30 and 40 minutes for all the four monomers viz., MMA, EMA, BMA and GMA respectively with TDEDB.

The effect of monomer concentration on the rate of polymerization was studied at various concentrations of monomers ranging from 0.8 to 1.8 mole dm$^{-3}$, by keeping the concentration of K$_2$S$_2$O$_8$, catalyst, ionic strength and pH as constant. Rp is found to increase with increase in concentration of the monomers.

The order of reaction with respect to monomer concentration is found to be 0.46 for MMA and EMA and 0.84 and 0.88 for BMA and GMA respectively. Also the plot of Rp versus concentration of monomer raised to suitable power passes through the origin in each case which confirm the above observations with respect to [RMA] using BEDDAB. With TDEDB the reaction order obtained for MMA and EMA are 0.48 and 0.55 and for BMA and GMA are 0.92 and 0.82 respectively.

The effect of concentration of K$_2$S$_2$O$_8$ on the rate of polymerization of RMA was studied by varying the concentration of K$_2$S$_2$O$_8$ in the range of 0.015 to 0.025 mole dm$^{-3}$ by keeping the concentrations of monomer, catalyst as fixed and at constant ionic strength, pH and volume ratio of aqueous to organic phase.
As the concentration of PDS is increased, Rp was found to increase in all the four systems when BEDDAB was used. From the plot of log Rp versus log \([K_2S_2O_8]\), the order of reaction is found to be nearly unity for MMA, 0.7 for EMA and 0.5 for both BMA and GMA. When the TDEDB was employed, the order of reaction is found to be 0.9 for MMA, 0.43 for EMA, 1.5 for BMA and 0.5 for GMA. The plot of Rp versus [PDS] raised to suitable power passes through the origin, supporting the above observation.

The effect of concentration of phase transfer catalysts, BEDDAB and TDEDB on the polymerization rate was studied by varying their concentration in the range 0.015 to 0.025 mol dm\(^{-3}\) at fixed concentrations of the monomer, PDS and at constant acid strength and ionic strength.

With increase in concentration of BEDDAB, Rp increased initially for all the four monomers, but it was found to decrease slightly as the concentration reached maximum. The order with respect to the concentration of the catalyst was found to be around 0.5 from the plot of log Rp versus log [BEDDAB] for all the four systems. The plot of Rp versus [PTC]\(^{0.5}\) is found to be linear passing through the origin confirming the above results. In the absence of PTC it has been observed that there was no polymerization reaction even after several hours.

A slight decrease in the rate of polymerization, which was observed as the concentration reached maximum may be due to steric hindrance of bulky benzyl group in the catalyst. This bulky group would have decreased the effective transfer of anion to the organic phase at higher concentrations. At higher concentration of the catalyst there will be interaction of the positively charged carbonyl carbon and the negatively charged oxygen atom with anion and cation of another catalyst molecule and this would have offered steric resistance for the transfer of anion to the growing chain. Therefore the rate does not increase beyond a limit due to which leveling off
tendency is observed. A plot of log Rp versus log [TDEDB] is found to be linear with the slope equal to 0.5 except for MMA indicating a half-order dependence of Rp on [TDEDB]. In the case of monomer MMA the order is nearly equal to unity with respect to PTC variation.

The effect of variation of volume fraction of aqueous phase with constant volume of organic phase on Rp has showed only a slight increase in Rp using both the catalysts. The rate of polymerization was found to increase with increase in temperature in all the four systems.

The effect of solvent on Rp was determined by carrying out the polymerization reaction for all the four monomers using BEDDAB and TDEDB, in three different solvents namely cyclohexane, ethyl acetate and cyclohexanone having the dielectric constants 2.02, 6.02 and 18.03 respectively. It was found that the increasing order of Rp in the solvents used follow the order, Cyclohexane < Ethyl acetate < Cyclohexanone. The increase in rate of polymerization may be due to increase in dielectric constants of the medium. It was found that ionic and acid strength has no significant influence on Rp values.

On comparing the molecular weights of the polymers synthesized using BEDDAB and TDEDB an increase in molecular weight is observed in the case of polymers synthesized by di-site phase transfer catalyst -TDEDB. In the case of single site PTC, the number of growing chains will be lesser than that of di-site PTC. Therefore when the concentration of monomer is kept constant, it is expected that higher molecular weight polymers with single site PTC than with di-site catalyst. But in the present study, high molecular weight polymer was obtained when di-site catalyst was used. This may due to the presence of benzoyl ethyl group in the single site PTC. This group might have offered steric resistance in the propagation step leading to leveling effect. When the concentration of single site catalyst is increased the
rate of polymerization tends to level off due to the same reason. Hence molecular weight of polymers synthesized using di-site phase transfer catalyst is high on comparing with the single site catalyst.

All the four alkyl methacrylates polymerized using single site catalyst- BEDDAB and di-site catalyst- TDEDB are compared by varying the concentration of monomers in the range of 0.8 to 1.8 mol dm$^{-3}$. Rp values were found to increase with increase in concentration of monomers. On comparing both the catalysts, slightly higher Rp is observed in case of polymers synthesized from TDEDB except in the case of MMA. For MMA Rp is more or less similar using both the catalysts.

In the case of single site PTC the number of anionic free radical provided by each catalyst molecule at a given time is one, where as in case of di-site PTC two anionic free radicals are provided by a single molecule. Hence at a time more number of growing chains can be seen in case of di-site PTC. Hence Rp is higher for di-site catalyst on comparison with single site catalyst.

The four alkyl methacrylates polymerized using single site catalyst and di-site catalyst are compared by varying the concentration of initiators 0.015 to 0.025 mole dm$^{-3}$ by keeping other parameters constant. Rp values are found to increase with increase in concentration of initiators. As expected, higher Rp is observed when the monomers were polymerized using disite catalyst.

Rp was determined and compared by varying the concentration of both the catalysts in the range of 0.015 to 0.025 mole dm$^{-3}$ by keeping other parameters as fixed. It is observed that, Rp values increased with increase in concentration of catalyst. However in case of single site catalyst as the concentration reached maximum a leveling tendency was observed hence Rp
decreased slightly. But in case of di-site catalyst no such effect was observed. Comparatively higher Rp is observed when the monomers were polymerized using disite catalyst.

On comparison, Rp was found to be more or less the same for both catalysts by varying the volume of aqueous phase with a constant volume of organic phase at fixed concentrations of monomer, PDS, PTC and at constant acid and ionic strength.

The dependence of temperature on the rate of polymerization was studied by varying its range from 50 °C to 65 °C by keeping the concentration of monomer, PDS, PTC as constant and at fixed ionic and acid strength. With increase in temperature the rate of polymerization was found to increase for all the four system using BEDDAB and TDEDB. Rp was found to be higher when di-site catalyst was used.

The synthesized polymers were characterized by FT-IR, thermal and X-ray diffraction studies.

The newly synthesized phase transfer catalysts have been employed for the free radical polymerization of vinyl monomers. Further these catalysts can be applied for organic reactions like alkylation, oxidation, reduction, addition, hydrolysis, etherification and esterification etc., and the hidden potentiality of these phase transfer catalysts can be explored progressively and their effectiveness on green chemistry can be further studied.