CHAPTER 1

INTRODUCTION

The concept of catalysis was first introduced by Berzelius in the year 1836. Later Ostwald defined a catalyst as a compound which increases the rate of a reaction, but which is not consumed by the reaction (Vassilis 2006). However, catalytic processes had been used long before this time, but since the concept of catalysis was not yet invented they were not recognized as such. Fermentation for example, had already been applied for thousands of years in brewing beer, and making wine and bread. In the middle ages sulphuric acid was synthesized, using nitrous vapors as a catalyst (Vansanten et al 1999). Our own body is one of the places were catalytic reactions play a very important role. Today catalysis plays a prominent role in our society, and the majority of all chemicals and fuels produced within the chemical industry have been in contact with one or more catalyst (Niemantsverdriet 2007). Catalysts are used to produce the desired products in a cheaper, safer, or for example environmentally friendlier way. Catalysis is of tremendous importance in many fields of applied chemistry, including the more traditional bulk / fine chemical synthesis and petro chemistry, as well as the more recent and still developing areas of environmental technology and energy generation/storage (Gates et al 2007).

The problem of bringing together two substances of markedly different polarities has been a continual challenge to chemists. Traditionally, it has been solved by using dipolar aprotic solvents in which the substances of different polarities are soluble. These solvents are however, expensive and
their low volatilities can make product purification tricky. Another more elegant solution to the problem is phase transfer catalysis, which allows substrates to come together without the need for a mutual solvent. Phase transfer catalyst can catalyze a number of organic reactions. Since the discovery of phase transfer phenomena in the late 1960s, many reviews on synthetic methods using phase transfer catalysts have been written (Starks 1994, Dehmlow et al 1993, 1998, Brandstrom 1997, Makosza 2000, 2003, Keller 1990, Yadav 2004).

1.1 PHASE TRANSFER CATALYST

A phase transfer catalyst can be defined as a substance, which increases the rate of reaction between substrates present in different phases. In this technique two mutually insoluble reagents, one being an organic phase other being aqueous phase react with the help of a phase transfer catalyst (Jing-Jer Jwo et al 2003). The phase transfer catalyst does the work of extracting the reactive anions from the aqueous phase and transfers them to the organic phase containing the reactant. Subsequently a reaction takes place between the transferred reagents and the non-transferred reactant within the organic phase.

1.1.1 Types of Phase Transfer Reactions

Since phase transfer catalysis deals with the reaction between immiscible phases, there are four situations where they are commonly used:

1. Liquid–liquid reactions
2. Solid -liquid reactions
3. Gas-liquid reactions
4. Triphasic reactions
1.1.1.1 Liquid-liquid reactions (LLPTC)

In this, an aqueous and an organic phase are in contact with each other. Phase transfer catalysis proceeds as per a two-step mechanism. The catalyst is present in the aqueous phase and transfers the reacting species (anion) across the interface what is called as the transfer step. The PTC thus makes the first reactant available to the second reactant in the organic phase and this is where the reaction occurs (Domenico 2003). This is the intrinsic reaction step. The anion displaced due to the reaction is carried back to the aqueous phase by the catalyst thus promoting the forward reaction in the organic phase. This mechanism is illustrated in Figure 1.1(a).

![Diagram](image)

**Figure 1.1** Two mechanisms for liquid-liquid reactions (Naik et al 1998)

(a) $Q^+$ soluble in the aqueous phase (b) $Q^+$ insoluble in the aqueous phase (1) Ion exchange (2) Organic phase reaction
According to a parallel mechanism for the same reaction, the PTC is soluble in the organic phase only and transfers the anions across the interface. This is illustrated in Figure 1.1(b). Both mechanisms are probably correct depending on the size of the PTC with the first being more likely for small and medium sized PTC’s and the second being predominant for medium and large PTCs (Starks 1997, Dehmlow et al 1995).

1.1.1.2 Solid-liquid reactions (SLPTC)

The function of solid liquid phase transfer catalysis is to conduct the reaction of a solid salt and the organic reactant using a phase transfer catalyst that is easily dissolved in the organic phases in the absence of water (Yang et al 2003). The most important step in phase transfer catalyzed reactions is that the catalyst must have the ability to transfer the reacting anion into the organic phase to react with the organic substrate. In the situation of the absence of water, the anion nucleophile should be given by the solid salt reactant, such that the unfavorable side reaction is probably inhibited. In addition, SLPTC can promote the weak nucleophiles, such as the salts of acetate, to have much higher reactivity by eliminating the hydrolysis effect (Naik et al 1998). Hence for SLPTC it has the advantages of easy separation of products from reactants, easy selection of organic solvents, easy recovery of catalysts, the inhibition or prevention of unfavorable side reactions etc., and shows great potential for commercial applications. Several reactions that cannot be performed in liquid-liquid phases can be carried out efficiently in solid liquid systems. Starks et al (1994) indicated that 100 per cent of the yield of product benzyl acetate was obtained at 25°C in two hours for the substitution reaction of potassium acetate and benzyl bromide using 18-crown-6 as the catalyst under SLPT conditions. This phenomenon of high conversion and product yield using SLPTC promotes more research work in investigating this type of reaction.
1.1.1.3 **Gas-liquid reactions (GLPTC)**

The organic substrate in gaseous state is allowed to pass over a bed consisting of the inorganic reagent which is coated with phase transfer catalyst in molten state. The gaseous reactant has to diffuse through the molten liquid film of the phase transfer catalyst, with reaction occurring simultaneously between the diffusion species and the catalyst. The advantages of GLPTC include ease of adaptation to continuous flow operation, absence of organic solvents since the organic substrate is present in gaseous form, ease recovery of the PTC and better selectivity for some reactions in comparison with LLP TC. Phosphonium salts, crown ethers and PEGs are the preferred catalysts used to carry out a variety of reactions under GLPTC. Separation of catalyst from the reaction mixture is easier in this case. Reaction is diffusion controlled and excess catalyst doesn’t affect the conversion.

1.1.1.4 **Triphasic reactions**

Since the first three types represent homogeneous catalysis, they pose a disadvantage of requiring an additional separation step to recover the catalyst. This recovery is important for the process to be cost effective, produce products of high purity and eco-friendly (Desikan et al 1995). This gave impetus to the development of PTCs immobilized onto solid supports and this solid support is the third phase – hence the name ‘triphasic’.

Triphasic catalyzed reactions hence can further be classified into three types depending on whether the inorganic reactant is in the solid, liquid, or gaseous phase (Montanari 1982).

- a) Liquid-liquid-solid reactions (inorganic reactant in the liquid phase)
b) Solid-liquid-solid reactions (inorganic reactant in the solid phase)
c) Gas-liquid-solid reactions (inorganic reactant in the gas phase)

The PTC can be conveniently separated from the reaction mixture and hence heterogeneous catalysis offers tremendous operational advantages. (Desikan et al 1995).

1.1.2  **Catalysts for Phase Transfer Reactions**

Agents used as PTC are

1) Onium salts (ammonium and phosphonium salts)
2) Macrocyclic polyethers (crown ethers)
3) Open chain ethers (polyethylene glycols and their dimethyl ethers, glymes)
4) Cyclodextrins

1.1.2.1  **Onium salts (ammonium and phosphonium salts)**

Quaternary onium salts are highly active and widely applicable in many PTC reactions. Quaternary ammonium salts are usually useful in neutral and acidic media up to 100-150°C (Ahluwalia 2007). Dequaternization of the quaternary onium salt by the reverse Menshutkin reactions occurs at elevated temperatures at non-basic media. Quaternary ammonium salts decompose by Hoffmann elimination, yielding the corresponding trialkyl amine and an alkene (Zerda et al 1986). Also in the presence of soft nucleophiles like RS-, R₃C-, R₂N-, RO-, nucleophilic SN₂ displacement on the quaternary cation is possible, liberating trialkyl amine as the leaving group and alkylating the nucleophile. Asymmetric quats are more active than symmetric quats due to
the lipophilicity imparted by the long chain alkyl groups (Starks, 1990). However in solid-liquid systems, where the quat has to approach the solid surface to pick up the reactive anion, symmetric quats perform better than asymmetric ones. Phosphonium salts, which are slightly more expensive than their ammonium analogs, are stable only under very mild conditions (Landini et al 1986).

1.1.2.2 Macrocyclic polyethers (Crown ethers)

Macrocyclic and macrobicyclic polydentate ligands like crown ethers and cryptands are widely used as phase transfer catalysts, especially in solid liquid systems, due to their ability to complex and solubilize the metal cations, along with corresponding anion to maintain charge. However, despite their high activity as effective PT catalyst, crown ethers and cryptand are not feasible for most industrial applications due to their high cost and toxicity. Crown ethers and cryptands are more stable at high temperatures and also in basic conditions and they therefore can be used up to temperatures of 120-150°C (Sasson et al 1997).

1.1.2.3 Open chain ethers (Polyethylene glycols and their dimethyl ethers, glymes)

Open chain ethers like polyethylene glycols and their many derivatives can be used as phase transfer catalyst (Totten et al 1998). They are relatively less costly and environmentally safe. Polyethylene glycols are stable, easy to recover, biodegradable and are easily available. Polyethylene glycols are very good phase transfer catalyst with activities better than that of crown ethers. Solubility in water makes them poor catalyst for liquid-liquid systems; although in cases the polyethylene glycol may forms the third catalyst rich phase and function as the active phase transfer catalyst.
1.1.2.4 Cyclodextrins (Cyclic oligosaccharide / polyalcohols of α-β-glucose with six to eight monomeric units)

Cyclodextrins form cylindrical like structure in aqueous solution having organophilic interiors and hydrophilic exteriors and form complexes with a large number of compounds and via the various intermolecular forces between host and guest molecules. Cyclodextrins can solubilize various organic compounds in aqueous phase solutions via formation of host guest complexes within the interior of the cyclodextrin structure; therefore, they are expected to be good candidates of inverse phase transfer catalysts.

Various other novel PT catalysts have been developed which find specific applications in certain types of reactions. For example, Kondo et al (1988) have developed polymeric analogs of dipolar aprotic solvents like dimethyl formamide, dimethyl sulfoxide, N-methyl 2-pyrrolidone, tetramethyl urea and so on in both cube and immobilized forms. Similarly Bhatacharya et al (1996) synthesized, chiral catalysts based on optically active amines like ephedrine, chinine and other cinchona alkaloids are widely used. Idoux and Gupton (1987) reported the use of polymer bound PT catalysts with more than one PTC site on the polymer. Similar multisite phase transfer catalyst can also be synthesized in their soluble non-polymeric forms from simple polyhalo substrates. Balakrishnan and Jayachandran (1995) reported the use of a new multisite PTC in the addition of dichlorocarbenes styrene. Advantages of a multisite catalyst include higher catalytic activity per gram of catalyst used, milder conditions and less contamination of product (Sanjeev and Doraiswamy 1998). Wang et al (2004) synthesized 1,4 bis (triethylmethylamonium) benzene chloride to synthesize dichlorocyclopropanone in an alkaline solution / chloroform two-phase medium.
Tomoyuki et al (2002) synthesized various a new asymmetric two-center phase transfer catalyst. The catalysts were applied in phase-transfer alkylations and Michael additions to afford the corresponding products upto 93 percent and 82 percent respectively. Wang et al (2002, 2004) synthesized two active catalyst 4,4- di – tetrabutylammonium biphenoxide produced and p-(tetrabutylammonium phenoxy) alkanoxy benzene using TBAB as the regenerated catalyst. Siva et al (2005) synthesized multisite phase transfer catalyst 1,3,5- tris (2-2,3-bis (triethylammoniummethylen chloride) phenoxy methyl benzene containing six active site for the first time using simple starting materials. N- butyl –N, N-dimethyl-α- phenylethylammonium bromide is prepared and used for various PTC reactions (Venkateshwar et al 2002).

1.1.3 Advantages of Phase Transfer Catalyzed Reactions

- elimination of organic solvents
- elimination of dangerous, inconvenient and expensive reactants
- high reactivity and selectivity of the active species
- high yield and purity of products
- simplicity of the procedure
- low investment cost
- low energy consumption
- possibility of mimicking counter current process
- minimization of industrial wastes

1.2 FREE RADICAL POLYMERIZATION

Free radical polymerization is widely used in industry; because generation of a radical is easy, many polymers can be polymerized, and
radical polymerizations are tolerant to the impurities (moisture, protic solvents), which normally would terminate an ionic polymerization. The drawback of radical polymerizations, however, is that while it is easy to generate a reactive radical that can initiate polymerization; the polymerization itself is difficult to control. A radical will readily react with the closest reactive site, either through disproportionation or through a coupling reaction. The former will produce both a saturated and an unsaturated chain end, while the latter will produce a single dead chain. Another major limitation for conventional radical polymerizations is that the molecular weight of the polymer chains is poorly controlled. Most free radical initiators have an initiator efficiency is less than unity. There have been attempts to remedy this situation. Chain transfer agents can be used to limit the molecular weight of the polymer. These additives react with the growing polymer chain, limiting the degree of polymerization without affecting the polymerization rate. Transfer agents can introduce functionality to polymer chain ends that will allow for post-polymerization reactions. Acrylate and methacrylate esters polymerize readily under the influence of heat, light and catalysts.

1.3 INITIATORS IN AQUEOUS MEDIA

1.3.1 Peroxide

Fenton’s reagent, the combination of H$_2$O$_2$ and ferrous salt, has been applied to the oxidation of many organic compounds, including alcohols, glycols, aldehydes, ethers, esters and amines. A mechanism for the reaction between hydrogen peroxide and ferrous ion involves a one-electron transfer from the ferrous ion to the peroxide with the dissociation of the oxygen–oxygen bond and the generation of one hydroxyl radical and one hydroxyl ion.

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow [\text{HO}^*\text{–OH}]\text{Fe}^{3+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^-
\]
In the presence of sufficient monomer, all of the \(^{\cdot} \text{OH} \) radicals generated can initiate polymerization. Polymerizations of several vinyl monomers, in aqueous media initiated by the H\(_2\)O\(_2\)–Fe\(^{2+}\) redox system, have been studied (Sarac 1999). Ferrous ions will promote the decomposition of a number of compounds, including alkyl and acylperoxides.

### 1.3.2 Persulfate (PDS)

Peroxodisulfate is a salt of peroxodisulphuric acid (Marshall’s acid); the most common salts are potassium peroxodisulfate and ammonium peroxodisulfate. PDS salts are water soluble, odourless, white crystalline solids, which decompose before melting. It is prepared by the electrolytic oxidation of the concentrated solution of sulfates at low temperatures.

\[
2\text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} + 2e^{-}
\]

They generate free radicals upon the thermally induced scission of O-O bonds, resembling the organic peroxides. Enhanced by the heat, light, or divalent metal as the catalysts, persulfate may decompose to produce sulfate radical (Huang et al 2002, Brown et al 2003). For potassium persulfates, the thermal decomposition rate constant is \(9.6 \times 10^{-5} \text{ sec}^{-1}\) at 80°C and the activation energy amounts to 130 KJ mol\(^{-1}\) (Liang et al 2003).

There are different reactions depending on the pH of the reaction media. In alkaline and neutral media, two radical anions are formed from one persulfate molecule. In strongly acidic surrounding, however, no radicals are generated, giving rise to a suppression of polymerization with lowering the pH.
The radical anion $\text{SO}_4^{-}$ can be generated by the photolysis (Clifton 1989) or thermolysis of the peroxodisulfate as well as by the one-electron reduction of peroxodisulfate (Gilbert 1990). The photolytic decomposition of PDS in aqueous solution at room temperature using 2537Å light gives rise to the evolution of oxygen as

\[ \text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O} \rightarrow 2\text{HSO}_4^{-} + \frac{1}{2} \text{O}_2 \]

The photochemical reaction is strongly inhibited by hydrogen and sulfate ion but is independent of acidity in the absence of sulfate ion. The evolution of oxygen in the decomposition of peroxodisulfate in water was studied by Beylerian et al (2002) using gasometric method. Similarly formation of $\text{SO}_4^{-}$ in the first step has been shown in the polymerization studies using PDS labeled with $\text{S}^{35}$ as initiator. The polymer fragments contains tracer sulfate end groups were isolated. No exchange of $\text{S}^{35}$ between sulfate and PDS was observed. This showed that first step is not reversible.

The peroxides were most commonly used for the polymerization of vinyl monomers and dienes into high molecular weight polymers. Peroxodisulfate alone can also initiate the polymerization but when silver ion is coupled with peroxodisulfate behaves as a powerful initiator and such catalytic effect has been investigated for several monomers (Manickam et al 1980, 1981). The rate of polymerization could be enhanced by using mixtures of peroxydisulphate, with oxidizing and reducing agents as initiator system. Polymerization initiated by the persulfate thiosulfate redox pair can be represented as

\[ \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^{-}, \ p\text{H} \geq 7 \]

\[ \text{S}_2\text{O}_8^{2-} + \text{H}^{+} \rightarrow \text{SO}_4^{2-} + \text{HSO}_4^{-} \quad \text{pH} < 7 \]
\[
\begin{align*}
S_2O_8^{2-} & \rightarrow 2SO_4^- \\
S_2O_8^{2-} + S_2O_3^{2-} & \rightarrow SO_4^- + S_2O_3^{2-} + SO_4^{2-}
\end{align*}
\]

The polymerization of acrylamide, acrylonitrile, methacrylamide and methyl methacrylate with persulfate (peroxodisulfate) and several different reducing agents has also been reported (Ariff et al 1985, Tajuddin et al 1986, Lenka et al 1981, Balakrishnan et al 1995). From kinetic studies with ascorbic acid involving acrylonitrile monomer, the formation of charge transfer complexes between ascorbic acid and persulfate was suggested. This produces ascorbate radicals for the initiation of polymerization. \(SO_4^-\) radicals produced via the thermal decomposition of \(S_2O_8^{2-}\) is considered to be responsible for the acrylamide polymerization. Mercaptans have been known as good redox pairs for vinyl polymerization, and recently \(\alpha\)-mercaptocarboxylic acids have been used as redox systems. PDS is also used alone as the sole initiator as in the case of aqueous polymerization of ethyl acrylate (Adhikari et al 1987) and acrylamide (Hunkeler 1991).

### 1.3.3 Peroxomonosulfate (PMS)

Potassium monopersulfate (KHSO\(_5\)), is a salt from the Caro’s acid \(H_2SO_5\). The oxidant undergoes both spontaneous and catalytic decomposition in acidic and alkaline media. The products of thermal decomposition are identified as oxygen and sulfate ions. The decomposition is found to be second order in total \([\text{PMS}]\) at 25°C and exhibits two types of acid dependence, viz. a direct first order dependence on acid concentration in the basic region and inverse first order dependence on acid concentration in the acidic region.

PMS exists as \(\text{HSO}_3^-\) in the pH range 6-8 and only \(\text{SO}_5^{2-}\) in the pH range greater than 10. Thompson (1981) observed that the combination of
Ag⁺ and PDS is an active catalyst for the decomposition of PMS and reported first-order dependence on PMS and first-order dependence on the catalyst. Thompson also reported first-order dependence on PMS with cobalt catalyst at pH: 0. Photolytic decomposition of potassium peroxomonosulphate was carried out by Kanakaraj and Maruthamuthu (1983). They observed first-order dependence on [PMS] with respect to photolytic exposure. The primary radical products SO₄⁻ and OH⁻ are formed by homolytic splitting of PMS. These were identified by syn-trapping agents such as fumaric and maleic acids.

Radiolytic decomposition of PMS has been studied extensively. Energetic radiation produces three reactive species in water (H⁺, OH⁻ and \( e_{aq}^- \)). It is inferred that both \( e_{aq}^- \) and OH⁻ are efficient in carrying out the decomposition of PMS. The formation of SO₅⁻ and SO₄⁻ radical product were identified by optical pulse radiolysis and oxygen as a molecular product was identified by mass spectrometry. The reaction responsible for the chain decomposition is the reduction of PMS by SO₅⁻ as follows:

\[
\text{HSO}_5^- + \text{SO}_5^- + \text{H}_2\text{O} \rightarrow \text{SO}_4^- + \text{SO}_4^{2-} + \text{O}_2 + \text{H}_3\text{O} \\
\text{OH}^- + 2\text{SO}_4^{2-} + \text{O}_2 + 2\text{H}^+
\]

1.3.4 Peroxodiphosphate (PDP)

\( \text{P}_2\text{O}_8^{4-} \) is electronically and isostructurally similar received relatively little attention till Levey and coworkers (1981) reported the photochemical oxidation of water, ethanol, propane-2-ol and some metal complexes by this ion. Gupta et al (1982) have studied the kinetics and oxidation of a large number of inorganic substrates by this ion. Since the
oxidation potential of peroxodiphosphate ion was found to be –2.07 V, which is very near to the oxidation potential of PDS (-2.01V). It is possible to predict that peroxodiphosphate might initiate vinyl polymerization like PDS through a radical mechanism. But surprisingly, not much has been reported on using PDP for initiating vinyl polymerization. Lenka et al (1980) have extensively studied the kinetics and mechanism of vinyl polymerization using a multitude of metal and non-metal ions. Very recently the use of peroxodiphosphate as initiator for graft co-polymerization of vinyl monomers onto wool, silk and cellulose fibers have been reported.

1.3.5 Alkyl Peroxodicarbonate (APD)

Most commonly, vinyl chloride polymerization is initiated by dialkyl peroxydicarbonates or their mixtures with peroxyesters. The initiation proceeds via by a generation of free radicals as a result of thermolysis (in some cases photolysis or presence of a redox system) of organic peroxide

\[(\text{ROCOO})_2 \xrightarrow{T\circ C} 2\text{ROCOO}^-\]

The heat sensitivity and rate of decomposition of peroxide generally depends upon the structure of the R group. Peroxydicarbonates are extremely reactive, decompose at moderate temperature and require a control temperature environment for shipping, handling and storage.

1.4 APPLICATION OF PHASE TRANSFER CATALYST TO POLYMERIZATION REACTION

Polymer synthesis using PTC include condensation polymerization, anionic polymerization and free radical initiated polymerization.
1.4.1 **Condensation Polymerization**

In polymerization process, the interfacial method should provide the highest molecular weight. The effect of retention time, mole ratio of the monomers, PTC on the yield and viscosity of the polymer are the main topics in polymer synthesis. PTC condensation polymerization resembles the mechanism describing an interfacial polymerization process. The polymers including polyesters, polythioethers, polycarbonates, polythiocarbonates, and others, can be synthesized via PTC condensation polymerization.

1.4.2 **Anionic Polymerization**

The anionic polymerization of n-alkyl ester of acrylic acid initiated by tetra-n-butylammonium alkyl and aryl thiolates produced quantitative yields of the corresponding polyacrylate. The case of the chiral macrocyclic multidentate ligands in the anionic polymerization of ethyl, t-butyl or benzyl esters of methacrylic acid initiated by potassium tert – butanoxide has also been reported. The polymerization depended critically upon the solvent, the best choice being acetonitrile, nitrobenzene and tetrahydrofuran. In the polymerization of n-butyl acrylate with tetra-n-butylammonium n-butyl thiolate, it was observed that polymerization continued with a quantitative formation of polymer having a slightly broader molecular weight distribution. Typical anionic polymerization processes are:

a) polymerization of n-alkyl esters of acrylic acid produced polyacrylate

b) polymerization of chiral macro cyclic multidentate ligands
1.4.3 Free Radical Initiated Polymerization

Potassium peroxodisulfate is a well-known free radical initiator for the polymerization of vinyl monomers in aqueous media. The use of this inexpensive initiator is limited because of its modest solubility in common organic solvents. The complex (1:2) of PDS and 18-crown-6 ether was found to be soluble in methanol, DMF, DMSO. Also polymerization can be carried out by PTC in the presence of initiator \( \text{K}_2\text{S}_2\text{O}_8 \)

\[
\begin{align*}
2\text{QX}_{(a)} + \text{K}_2\text{S}_2\text{O}_8 & \quad \leftrightarrow \quad 2\text{KX} + \text{Q}_2\text{S}_2\text{O}_8 \\
\text{Q}_2\text{S}_2\text{O}_8\text{a}(a) & \quad \longrightarrow \quad 2\text{Q}^+\text{SO}_4\cdots\text{(a)} \\
\text{Q}_2\text{S}_2\text{O}_8\text{a}(a) & \quad \longrightarrow \quad \text{Q}_2\text{S}_2\text{O}_8\text{o}(o) \\
\text{Q}_2\text{S}_2\text{O}_8\text{o}(o) & \quad \longrightarrow \quad 2\text{Q}^+\text{SO}_4\cdots\text{o}(o) \\
\text{Q}^+\text{SO}_4\cdots\text{o}(o) + 2\text{M}_\text{o}(o) & \quad \longrightarrow \quad \text{M}^\cdots \\
\text{M}^\cdots + \text{M} & \quad \longrightarrow \quad \text{M}_2^\cdots \\
\text{M}_{n-1}^\cdots + \text{M} & \quad \longrightarrow \quad \text{M}_n^\cdots \\
2\text{M}^\cdots & \quad \longrightarrow \quad \text{polymer}
\end{align*}
\]

where \( X \) is Cl, Br, HSO\(_4\) etc and the subscripts "\text{o}" and "\text{a}" refers to the organic and aqueous phase.

The water-soluble free radical initiator and the phase transfer catalyst form an organic soluble complex, which is soluble in organic liquid wherein, upon activation of the free radical initiator, free radical polymerization is initiated. This method of delivering free radical catalyst to the organic phase containing the monomer provides a unique degree of control over the free radical polymerization reaction rate.
The water-soluble initiators are generally more stable and therefore present fewer storage and handling problems. Polymerizations can be carried out at substantially lower temperatures and in much shorter reaction times. This surprising feature provides a tremendous advantage, especially in bulk or high solids solution polymerizations, in reducing problems associated with heat dissipation. Shorter reaction times also have their economic advantages.

A number of reports have appeared on the influence of phase transfer catalyst e.g. crown ethers on anionic polymerization. Rasmussen and Smith (1981) reported many examples of free radical polymerizations under phase transfer conditions with aqueous persulfates and found this method to be more facile than when common organic soluble initiators were used. Rasmussen and Smith (1984) observed a ten fold increase in shear strength of iso octyl acrylate and acrylic copolymers prepared by phase transfer free radical polymerization. There is also a report that the polymerization with phase transfer catalyst can be conducted at low temperature with high reaction rate. Kunieda et al (1984) used cyclodextrins as phase transfer catalysts in the polymerization of water soluble monomers for transferring initiators soluble in organic solvents into aqueous media containing the monomers. Polymerization of a number of water-soluble monomers was carried out using different organic soluble initiators in water / chloroform two-phase system. It was found that the methylated β- cyclodextrin accelerated the polymerization of aryl group containing water insoluble monomers, using water-soluble initiators in a two-phase water / chloroform system. Takeishi et al (1998) studied the reactivity and the structure of alkyl methacrylates.

Jayakrishnan (1983) and Ghosh (1990) et al have also studied the kinetics of phase transfer catalyst systems for transfer of radical anions or peroxy-anions for initiation of polymerization. Choi and Lee (1987) found that poly methyl methacrylate prepared by phase transfer catalyst had higher
molecular weight and more uniform molecular weight distribution than that prepared by azobisisobutyronitrile (AIBN).


Vajjiravel et al (2007, 2008) have reported kinetic study of polymerization of vinyl monomers using potassium peroxodisulfate as initiator in the presence of disite phase transfer catalyst.

The study of literature of all the phase transfer catalyzed system with water-soluble initiator reveals that the transfer of active species from one phase to the other phase involves the initiation step of free radical polymerization. The polymers prepared by PTC exhibit higher molecular weight with constant polydispersity.

1.5 SCOPE AND OBJECTIVE

The phase transfer catalyst reactions find wide application in all branches of chemistry especially in oxidation, reduction, polymerization, and reactions of carbene, addition reaction, condensation and so on. The study of phase transfer catalyst assisted free radical polymerization is one of the fields of interest. High molecular weight polymers with good shear strength can be obtained by this technique. In kinetic aspect, the overall rate of polymerization is high even under mild reaction conditions.
There is a vast scope for further work on this technique to the extension of its industrial applications as well as the investigation of the kinetic and meschanistic aspects of the phase transfer catalyst assisted free radical polymerization.

It is proposed to synthesize two new phase transfer catalyst, characterize and use further for the polymerization of three monomers using the catalyst and water-soluble free radical initiator. Our main aim is to study the kinetics of polymerization of the monomers, methyl methacrylate, ethyl methacrylate, butyl methacrylate and to find out the synthetic route for the preparation of high molecular weight polymers.

The other objectives set forth for the present investigation are

1. to study the effects of varying concentration of monomer, phase transfer catalyst and peroxomonosulfate, ionic strength and temperature on the rate of polymerization
2. to find out the efficiency of the catalyst in catalyzing free radical polymerization
3. to propose a suitable mechanism and to derive rate expression based on the kinetic results
4. to evaluate the overall energy of activation for polymerization and other thermodynamic parameters
5. to determine the degree of polymerization to support the proposed mechanism
6. to characterize the polymers by infrared radiation spectroscopy, differential scanning calorimetry, thermogravimetric analysis and X ray diffraction studies.