CHAPTER 1

INTRODUCTION

Polymers are of great interest for science and industry as they are the most extensively used material in day-to-day life. Annual production of polyolefins is reported to be around 322 million metric tons in 2015. The increase in polyolefin production was triggered by the discovery of heterogeneous catalysts primarily based on titanium tetrachloride and diethylaluminium chloride as a counteranion [1].

1.1 Types of Polymerization Catalysts

1.1.1 Heterogeneous Catalysts: Heterogeneous catalysts are the type of catalysts which are found to be in different phase from that of the reactants. Early transition metal halides are the active catalysts supported by MgCl₂ with a high surface area. Microporous spheres of amorphous silica is the another component of the heterogeneous catalysts, which is used as a carrier. All these catalysts are activated with organoaluminum compounds such as Al(C₂H₅)₃. Heterogeneous Ziegler-Natta catalysts have been successful for polymerization of olefins and have many industrial applications because of their ease of separation which often results in lower cost of catalyst losses. Despite these advantages, due to the presence of different active sites [2], heterogeneous catalytic systems fail to influence the polymer microstructure to larger extent and results in polymer with broader polydispersity index. Moreover, the polymerization mechanism is ill-defined and the residue on the surfaces of the catalyst may poison and block the active sites of the catalysts. To overcome these problems the era of homogeneous metalloocene complexes came to existence.

1.1.2 Homogeneous Catalysts: Metallocene complexes are the second broader class of polymerization catalysts which are reported to be soluble in reaction medium. Homogeneous catalysts show only identical active sites with less chance of substrate poisoning. These advantages result in the production of polymers with high selectivity and narrow molecular weight distribution [3]. Initially these homogeneous metallocene complexes along with alkylaluminium cocatalysts were used for polymerization but with low activity.

\[ \text{Cp}_2\text{TiCl}_2 + \text{AlR}_2\text{Cl} \rightarrow \text{Low activity} \]
In 1977, the discovery of new cocatalyst, methylaluminoxane brought new startup for the transition metal complexes [4]. MAO plays crucial role in polymerization, as it is found to be quite effective to enhance the catalyst activity towards polymerization reactions.

\[
\text{Metalloocene + Methyl Aluminoxane} \rightarrow \text{Very high activity}
\]

Brintzinger et al. in 1982, set another milestone by synthesizing highly active chiral bridged metallocene catalysts. Meanwhile, Walter Kaminsky introduced the zirconocene catalysts capable of producing highly stereoregular polymeric materials [5]. Encouraged by the progress of metallocene complexes, half-sandwiched complexes had also been introduced. In mid nineties research interest switched from cyclopentadienyl to non-cyclopentadienyl ligand system to avoid the growing patent minefield in group 4 cyclopentadienyl complexes and to study the potential of the other transition metal complexes towards homo and copolymerization of α-olefins. As a result of enormous amount of academic and industrial research in this direction, a diverse array of new, highly potent catalysts based on early and late transition metals have been discovered, capable of producing polymers with distinctive properties e.g., hyperbranched polyethylene, ethylene/methyl acrylate copolymers, block copolymers etc.

Development of new catalysts for copolymerization of ethylene and polar olefins is another challenge in the field of polymerization due to oxophilicity of early transition metals. Hence, late transition metals are targeted more for the synthesis of copolymers. Complexes of late transition metals like palladium, nickel, iron and cobalt activated by MAO were reported for the copolymerization of olefins. Di-imine Pd(II) and Ni(II) dimethyl cationic species, introduced by Brookhart, are the most widely used complexes for copolymerization of ethylene and propylene with functional vinyl monomers [6]. Changes to ligand framework by using different substituents provide access to polymer products with new and versatile properties.

1.2 Ligand based Metal Catalysts

1.2.1 Types of Ligand

Denticity refers to the number of donor groups in a single ligand that binds to the central atom. Depending on the binding ability of the ligand to metal centre to form a coordination complex, ligands are of various types as follows:
1.2.1.1 **Monodentate:** Monodentate ligands have only one atom capable of binding to a central metal atom or ion. For example, \( \text{H}_2\text{O} \), \( \text{CO} \), \( \text{NH}_3 \) etc. are neutral and \( \text{F}^- \), \( \text{Cl}^- \), \( \text{Br}^- \), \( \text{I}^- \) and \( \text{CN}^- \) are negatively charged monodentate ligands.

1.2.1.2 **Polydentate:** A ligand molecule with more than one donor atom is called a polydentate ligand. Depending on the number of donor atoms they contain, they may be bidentate, tridentate, tetradentate and so on. For example, phenoxy-imine \([\text{N, O}]\) [7], phenoxy-ether \([\text{O}^-\text{O}]\) [8], phenoxy-thioether \([\text{O}^-\text{S}]\) are bidentate ligands. Tridentate ligands contain three donor atoms e.g. bis-(alkoxide) \([\text{O}^-\text{NO}]\) [9], phenoxy-imine bearing diphenylphosphorous group \([\text{NOP}]\) [10], arylsulfide \([\text{O}^-\text{NS}]\) [11] ligands, whereas diphenolate \([\text{OSSO}]\), amine bisphenolate \([\text{ONNO}]\) [12] and salen \([\text{ONNO}]\) [13] are the example of tetradentate ligands.

1.2.1.3 **Ambidentate:** Ligands that can bind through two possible sites. For example, the thiocyanate ion \((\text{SCN}^-)\) can bind to the central metal either through the sulfur or the nitrogen atom.

Numerous postmetallocene catalyst precursors for olefin’s polymerization have been developed. Amidinate [14], oxazolin [15], porphyrin [16], alkoxy [17] and many more ligands were used for their synthesis but proved to be less active. Fujita and Coates developed an important family of highly active group 4 metal complexes bearing phenoxy-imine [18] frame work which are reported to be a class of catalysts, found to catalyze living polymerization and produce high molecular weight ethylene and stereoregular polypropylene.

### 1.3 Side Arm Effect

Side arm effect is another strategy which is used in the recent years to modify the metal catalysts. The significance of hard \((\text{N, O})\) and soft \((\text{S, P})\) donors has been reported by Kakugo [19], Kol and Coworkers, Goldschmidt [20] and many more. Recently, their use for synthesizing metal catalysts has been emphasized more due to their important role in determining the rate of propagation and rate of termination. The pendant donor has also proved to play key role in achieving high activities. Till date ligands bearing hard pendant donors have emerged to develop transition metal catalysts. The use of soft pendant donors for ligand synthesis and their use for synthesis of complex containing mid-to-late transition series is not promising due to hard-soft mismatch of hard metal and soft donor in a catalyst system.
Despite this, complexes bearing soft donors have been reported to be more efficient in catalyzing polymerization reactions in comparison to hard donors. On the basis of efficient role of side arm appended heteroatom groups like nitrogen, oxygen and sulphur, number of tri [O-NX] [21] and tetradeutate [ONNO] [12] ligands bearing metal complexes were reported. The effect of substituent attached to ligand system also play important role on catalyst activity, average molecular weight and PDI value.

1.3.1 Types of Non-Cyclopentadienyl Ligands with Side Arm

1.3.1.1 Diamide Ligands: Chelating diamide titanium complexes (Figure 1.1) bearing bulky substituents [22] have been reported to be highly active catalysts for the production of polyolefins. Ti(IV) dimethyl complexes activated by B(C$_6$F$_5$)$_3$ has been reported to catalyze polymerization of 1-Hexene in a living fashion at ambient temperature condition. But the activity of the catalyst has been reported to be low. Therefore, with the aim of forming more stable metal complexes, chelating diamide ligands with additional donors have been investigated. The complexes with additional donor atoms were reported to catalyze polymerization of 1-Hexene with narrow PDI, in combination with suitable borane activators [23].

![Figure 1.1: Diamide based metal complexes](image1)

1.3.1.2 Salicylaldiminato ligands: Ti(IV) complexes (Figure 1.2) containing salicylaldiminato ligands with pendant donor shows higher activity than the corresponding catalyst without side arm. Similarly nickel complexes bearing salicylaldiminato ligands with carbene as pendant donor were also reported [24].

![Figure 1.2: Salicylaldiminato based metal complexes](image2)
1.3.1.3 Phenoxy-ether Ligands: Extensive study has been made on catalysts bearing nitrogen as neutral donors (imine, pyridine). To provide alternate to nitrogen donor for pyrrolide, indolide and phenoxy based ligand, chelating phenoxy-ether [18] ligand based complexes (Figure 1.3) has been introduced. These were reported to exhibit polymerization efficiency comparable to that of phenoxy-imine based metal complexes.

![Figure 1.3: Phenoxy-ether based metal complexes](image)

1.3.1.4 Phenoxy-amine Ligand: Kol and coworkers introduced a successful class of phenoxy-amine based metal catalyst (Figure 1.4) for 1-Hexene polymerization [25]. The activity of the complex has been reported to be moderate in absence of donor atom but with addition of donor group, Ti(IV) complex polymerizes 1-hexene in living fashion and also reported to synthesize block copolymers [26].

![Figure 1.4: Phenoxy-amine based metal complexes](image)

1.4 Polymerization Techniques

Initially catalytic polymerizations were carried out mostly in organic solvents. Increasing environmental concern regarding the detrimental effect of volatile solvents made the researchers more curious about the catalytic aqueous polymerization.

Only late transition metal complexes were capable for catalyzing aqueous polymerization. However, in these cases, due to the ease of β-hydride elimination [27], usually low molecular
weight polymers are obtained. Manders et al. was the first to report the use of early transition metal catalysts in aqueous polymerization of styrene [28]. However, only little attention has been given to aqueous polymerization, catalyzed by early transition metal catalysts bearing pendant donors.

1.4.1 Types of Aqueous Polymerization on the Basis of Nature of Dispersed Media

Polymerization in aqueous media is the most environmental friendly, economic and nontoxic approach to carry out polymerization reactions and to prepare polymer particles with a variety of size. Different techniques were studied to carry out aqueous polymerization. Generally in these processes water act as a continuous phase and monomer/polymer in the form of fine dispersion in water. These techniques have been distinguished on the basis of starting materials, kinetics of polymerization, particle formation and finally on the size of polymer particle.

1.4.1.1 Suspension Polymerization: Radical initiators are used mostly to carry out suspension polymerization. In this type of polymerization, initiators are soluble in monomer phase, which is dispersed usually in water to form droplets. Suspension polymerization favors the synthesis of polymer beads in the range of 10μm-0.5mm [29].

1.4.1.2 Emulsion Polymerization: Emulsion polymerization is applicable to slightly water soluble or insoluble monomers. Emulsion polymerization is commonly used for vinyl monomers undergoing radical polymerization. The monomer is emulsified using surfactant as an emulsifier. In the initial stages monomers are present in the size range of 1-10μm or larger droplets and small amount of monomers exist in surfactant-solubilized micelles. The polymer
particles are formed via nucleation. The monomers consumed for the synthesis of polymer particles drives the diffusion of monomers from monomer droplets to micelles having growing polymer chains. Polymer particles in the range of 50-500nm is formed [30].

1.4.1.3 Miniemulsion Polymerization: This technique is used to overcome the limitations of the emulsion polymerization. All the components, radical initiator or lipophilic catalyst (dissolved in small amount of organic solvent), hydrophobe (e.g. hexadecane) and aqueous surfactant solution [31] are premixed followed by the homogenization to stop the transfer of monomers from small droplets to large droplets to reduce surface energy and to produce polymer material with narrow polydispersity. Co-stabilizer is used to stabilize the whole system so that the polymer particle formation is initiated.

1.4.1.4 Microemulsion Polymerization: Microemulsion is an optically transparent system with thermodynamic stability. The process involves the mixing of monomers and water in presence of appropriate amount of surfactant without any homogenization. The polymerization started with the entry of initiator into the micelle containing monomer called as “monomer-swollen micelles”. Some of these micelles are subsequently converted to polymer particles during the polymerization. Polymer particle grows further by the transport of monomers from outer phase. Ultrafine latex particles within the size range of 10-100nm is prepared using microemulsion technique [32].

1.5 Polymerization of Acrylates

Fox et al. and Miller et al. were the first to prepare stereoregular acrylates using variety of aluminum, magnesium and lithium compounds [33]. Later on radical and anionic initiators were also reported to synthesize stereocontrolled poly(acrylate)s (Scheme 1.1). At commercial level, free radical initiators are used to synthesize polyacrylates but due to limited scope of stereocontrolled polymer products, interest has been switched to catalytic polymerization. Group 4 metal complex Cp₂ZrCl(OC(OMe)=CMe₂) was reported to polymerize MMA in living fashion. Collins and Ward [34] also confirmed the synthesis of PMMA using Cp₂ZrMe₂ complex, with narrow PDI (1.2-1.4) value along with a syndiotactic character in comparison to free radical polymerization. Cyclopentadienyl titanium complexes were also reported to carry out aqueous homopolymerization of MMA at ambient temperature.
1.5.1 Properties of Polyacrylates

Polyacrylates are the class of polymers generally called as plastics. Polymethyl methacrylate is also known by trade names Plexiglass [34], Acrylite, Lucite and Perspex. The polyacrylates are always noted for their transparency, resistance to breakage, elasticity and high surface resistivity. Due to these outstanding characteristics, polyacrylates has been used commercially as additive, coating and polishing agents, binder and optical fibers. Acrylic paints are also famous as an artist’s paints.

1.6 Polymerization of Styrene

Polystyrene is the most widely used nonpolar polymer after polyethylene. Polystyrene can be prepared by all the conventional mechanisms, radical, cationic, anionic and coordination-insertion catalysis (Scheme 1.2). Heterogeneous Ziegler-Natta catalysts were used initially to develop polystyrene. Later on metallocene systems were used as a method of choice, for controlling microstructure of PS. In 1955, Natta used TiCl₄/AlR₃ binary systems to synthesize isotactic PS for the first time. Ishihara et al. [35] was the next to develop syndioselective polystyrene using homogeneous titanium half-sandwich catalysts.

In addition to homopolymerization, copolymerization of polar and nonpolar olefins was also a major question of concern due to extreme oxophilic and halophilic nature of early transition metal catalyst, which make them incompatible with functional vinyl monomers. Only late transition metal complexes were studied well in this regard. Patra et al. synthesized high molecular weight homo and copolymers of styrene and MMA using Cp₂MCl₂ (M =Ti or Zr).
Aqueous copolymerization of (Styrene and MMA), catalyzed by CpMCl$_3$(M =Ti or Zr) was reported by Yan et al. Later [ONO] based titanium complexes were also found to synthesize high molecular weight homo and copolymers, poly(Styrene$\text{co}$MMA) in aqueous emulsion at ambient temperature condition.

1.6.1 Properties of Polystyrene

PS is often used in products that require clarity, such as food packaging and laboratory ware. When combined with various colorants, additives or other plastics, polystyrene is used to make appliances, electronics, automobile parts, toys, gardening pots and equipment and more. Polystyrene is also used as a foam material, called expanded polystyrene (EPS) or extruded polystyrene (XPS), which is valued for its insulating and cushioning properties.

1.7 Scope for the Present Study

Over the past two decades number of late transition metal catalysts has been investigated to carry out aqueous polymerization reactions such as polymerization of conjugated dienes [36], vinylic polymerization of cyclic olefins, ring opening metathesis polymerization, polymerization of alkynes [37], copolymerization of carbon dioxide with olefins and many more, as these late transition metal catalysts [38] offers less oxophilicity and good tolerance towards functional group monomers. Extensive research for developing early transition metal catalysts has been restricted due to halophilicity, Lewis acidity and easy deactivation and decomposition of well known Ziegler or Philips catalysts even in the presence of trace amount of moisture. However, a survey on the aqueous solution chemistry and stability of the early transition metal complexes reveals the all the early transition complexes are not that much unstable in water as they thought to be. In fact there are number of reports in support of moderate to high aqueous stability of early transition metal complexes. These complexes remain stable in aqueous medium for sufficiently long time to carry out polymerization
reactions. Early transition metal based metallocene complex, bispentamethylcyclopentadienyl titanium dichloride is reported to possess some anticancer activity. To study the stability and hydrolysis chemistry of metallocene dichloride complexes M(\eta^5-C_5H_5)_2Cl_2, (M = titanium, vanadium and zirconium), Marks et al. [39] carried out number of research and found that addition of any of the Cp_2MCl_2 complexes to water results in rapid chloride hydrolysis. It was also found that the \eta^5-C_5H_5-M bond is moderately stable in water and cyclopentadiene ring protonolysis follows first order kinetics with half-life of \sim 10 days for Cp_2VCl_2, \sim 57h for Cp_2TiCl_2 and \sim 14h for Cp_2ZrCl_2 at 37^\circ C. Therefore, in unbuffered solutions, the metallocenes are expected to have stable metal-ligand bonds over a number of days. The pH of unbuffered aqueous solution of Cp_2TiCl_2 which is found to be \sim 3, the pK_a value of 3.5 and 4.35 for the Cp_2Ti^{2+} bound water molecules suggest, [Cp_2Ti(OH)_2]^2+ and Cp_2Ti(OH)(OH_2)] to be the most abundant species present in the solution (Figure 1.5).

![Figure 1.5: Various species present in equilibrium in an aqueous solution of Cp_2MCl_2](image)

Therefore, assuming that the kind of equilibrium shown in Figure 1.6 exist between monomer and water, polymerization involving [Cp_2Ti(OH)(OH_2)]^+ as an active cationic species may exist in aqueous solution. In fact, existence of this kind of equilibrium in case of late transition metals had already been proved experimentally and theoretically by catalyzing ethylene polymerization in aqueous medium. As water also competes with incoming monomers for coordination site but it has been reported that for late transition metal catalyst, Ni and Pd, the ethylene coordination is preferred over water and hence chain growth continues even in presence of water [40].
Environmental friendly approach to synthesize polymeric material grew researcher’s interest to synthesize water soluble and stable complexes. In addition to metalloocene complexes, number of postmetallocene complexes have been developed which are reported to have higher catalytic activity towards aqueous polymerization reactions [41].

Aqueous polymerization reactions catalyzed by transition metal complexes need counteranions to stabilize the active cationic metal centers. Methylaluminoxane is used extensively to stabilize the active cationic metal species in non aqueous medium but due to its moisture sensitivity, toxicity and expensiveness, for aqueous polymerization one must find some alternative water soluble and stable cocatalysts or a catalytic system which do not require any activator/cocatalyst. In 1986, Jordan et al. prepared the complex, [(Cp₂ZrMe(THF))⁺[BPh₄]⁻ having ability to polymerize ethylene in the absence of cocatalyst [42]. Moreover, the search for counteranion free catalytic polymerization continued and Manders et al. in 2001 reported the use of cocatalyst free metal complex [(C₅Me₅)Ti(OMe)₃] for aqueous polymerization of styrene [29]. In addition to this, Cp₂MCl₂ (M= Ti and Zr) complexes stabilized by soft and weakly coordinating tetraphenyl borate counteranion have been reported to catalyze aqueous polymerization of polar and non polar olefins at room temperature. A 14-electron cationic species [Cp₂M(OH)]⁺ may be the actual catalytic active species which can produce high molecular weight homo and copolymers [43].

Recently, there has been a growing interest in post metalloocene complexes catalyzing aqueous polymerization of α-olefins. A phenoxy-amine based Ti(IV) metal complex is reported to be the first example of room temperature aqueous emulsion polymerization by early transition metal based nonmetalloocene catalyst [44].

Side arm approach is another instrumental technique used in recent years to improve the catalytic activity [55]. The hard and soft donors provide higher stability and extraordinary catalytic activity for polymerization mostly in organic solvents. Inspired by the success of [ONO]-type phenoxy-amine based metal catalyst in aqueous polymerization, this thesis
presents the author’s successful efforts in the development of a water stable, new postmetallocene early transition metal complex which is cheaper, easier to synthesize and can efficiently polymerize styrene and MMA. To study the effect of extra donor groups on catalyst activity, two more phenoxy amine based [ONNO] and [ONSO]-type metal complexes have been synthesized and their effectiveness in the aqueous homo and copolymerization of acrylates at ambient temperature have also been investigated in detail.

1.8 Objectives of the Thesis

Continued demand of new and valuable polyolefin products for sure will go on to progress continuously for many coming years. Even though metal complexes catalyzed olefin polymerization is a mature field, there is no single class of catalyst design which are reported to be stable, inexpensive along with high activity, stereoregularity and regioselectivity. Moreover, in past 50 years the polar polyolefin copolymers such as ethylene–methyl acrylate (EMA) or ethylene–vinyl acetate (EVA) are synthesized by radical initiators under high temperature and pressure due to intolerance of Ziegler-Natta catalysts towards polar monomers. The resulting polymer materials have major drawbacks, having broader molecular weight distributions along with branched polymer structure. Modification in catalyst design may prove to be a key success and permits the copolymerization of polar and nonpolar olefins under mild condition and allow microstructure control of copolymer products.

Hence, we were interested to develop new and novel post-metallocene titanium(IV) metal complexes very conveniently at comparatively cheaper rate along with moderate stability for carrying out polymerization reactions in aqueous medium. In case of radical polymerization energy cost is higher, so we were interested to carry out all polymerization reaction at ambient temperature condition to reduce the energy cost.

Recently, there has been a growing interest to develop new post-metallocene catalysts and to understand the factors that control the molecular weight, comonomer incorporation and show ever-higher catalyst productivity. Such attempts have resulted in the discovery of highly active catalysts such as pyrrolide-imine, indolide-imine and many more, FI catalyst is one of the most active complex among them. However, all these metal precursors were reported to be activated by hazardous alkyl aluminium activators and found to stable only in organic solvents.
Copolymerization of nonpolar with polar alkenes has been reported to enhance the properties of the polymer product such as adhesion, solvent resistance, surface properties and many more. Therefore, another objective of present work to carry out homo and copolymerization of polar and nonpolar as well as polar olefins such as poly(Styrene-co-MMA) and poly(MMA-co-MA) using phenoxy-ether type and phenoxy-amine based titanium(IV) complexes activated by large, soft and weakly coordinated counter anion (tetraphenyl borate). Million tons of surfactant-stabilized polymer latexes are produced annually using emulsion polymerization techniques. These stable polymer particles have number of applications in the medical, biological and industrial processes. Hence, we were also interested to study characteristics of the polymer latex using differential instrumental techniques such as FESEM, HRTEM and DLS. Efficacy of catalysts play significant role in polymerization process. Kinetics parameters such as rate constant and activation energy are of importance to study the catalyst activity and stability. Hence, another objective is to study and compare the different kinetic parameters of newly synthesized catalysts with free radical polymerization initiators.