CHAPTER II

LITERATURE REVIEW

The first homogeneous metallocene catalysts were discovered in 1957 by Natta [15] and Breslow [16], who used bis(cyclopentadienyl)titanium-(IV) compounds together with aluminium alkyls for ethylene polymerization. These catalysts systems, replacing the chloride ligand of the Ziegler-Natta transition metal catalyst system by cyclopentadienyl (Cp) derivative compounds, were mainly used in mechanistic studies [17,18]. Subsequently, Kaminsky and his co-workers found that the addition of water to the trialkyl aluminum in a molar ratio of 1:1 during ethylene polymerization significantly increased the catalytic activity [19,20]. The reaction of trialkyl aluminum with water was shown to produce alkyl aluminoxane. In 1980 Kaminsky and coworkers [19] used oligomeric methyl alumoxane (MAO) with group 4B metallocene compounds to obtain ethylene polymerization catalysts having extremely high activities. For instance Cp_2TiCl_2/MAO has polyethylene productivity of $9.3*10^6$ gPE/ (mol Ti·hr·atm) at $20^{\circ}C$; the productivity is $9*10^7$ gPE/(mol Zr·hr·atm) at $70^{\circ}C$ with Cp_2ZrCl_2/MAO. However, these catalysts are non-stereospecific producing only atactic polypropylene, because of the symmetric feature of their active centers.

In the early 1980s Brintzinger and coworkers synthesized racemic ethylene-bridged bis(indenyl)zirconium dichloride, $Et(Ind)_2ZrCl_2$, and racemic ethylene-bridged bis(4,5,6,7-tetrahydroindenyl)zirconium dichloride, $Et(H_4Ind)_2ZrCl_2$ [21], as well as their titanium analogues, $Et(Ind)_2TiCl_2$ and $Et(H_4Ind)_2TiCl_2$ [22], which have both meso and racemic configurations. The steric rigid chiral $Et(Ind)_2ZrCl_2$ and $Et(H_4Ind)_2ZrCl_2$ catalysts activated with MAO catalyzed the stereoselective polymerization of propylene with very high activities. It was the first time that the isotactic polyolefins were obtained from homogeneous Ziegler-Natta polymerizations. This finding demonstrated stereochemical control by the chiral ansa-indenyl ligands on the transition metal ion in the selection of one of two enantiotopic faces (re or si) of a prochiral vinyl monomer in migratory insertion. As predicted, the meso-$Et(Ind)_2TiCl_2$/MAO system only produced atactic polypropylene. Since then a large

group of ansa-metallocene compounds have been developed each of them having unique catalytic activity and stereospecificity.

The discovery of the ansa-metallocene catalysts is believed to be of immense significance to the catalytic, organometallic and polymer sciences. The structure of a metallocene can be determined by X-ray diffraction. Modification of catalysts by variation of the ligands surrounding the active center permits a correlation of catalyst structure with catalytic activity and stereospecificity. Studies made on such metallocene compounds have increased our understanding of the molecular mechanism of stereochemical control in α-olefin polymerizations. It is believed that the true active species in the metallocene/MAO system are electrophilic 14-electron metallocene cations [23]. Most probably the cations do not exist freely, but rather are solvated in some way by MAO [24].

More recently, cationic metallocene catalysts have received growing interest as model systems for homogeneous MAO activated metallocene catalysts. The research on this topic began with the work of Jordan et al., [25] who demonstrated in 1986 that the zirconium complex $[Cp_2ZrCH_3(THF)]^+[BPh_4]^-$ (Ph = phenyl) polymerizes ethylene in polar solvents. Subsequently, it has become possible to develop cationic metallocene catalyst systems which polymerize ethylene, propylene and higher α-olefins with high activity even in non-polar solvents such as toluene. These systems are composed of Lewis base-free zirconocene cations with fluorinated or perfluorinated $[BPh_4]^-$ or suitably substituted carboranes as counterions [24]. The most promising system among them was developed by Chien et al. [27]. The metallocene cation $[Et(Ind)_2Zr(CH_3)]^+B(C_6F_5)_4^-$, formed by the reaction of $Et(Ind)_2Zr(CH_3)_2$ with triphenylcarbenium tetrakis(pentafluorophenyl)borate, $Ph_3C^+B(C_6F_5)_4^-$, showed a higher activity and similar stereospecificity when compared to the $Et(Ind)_2ZrCl_2$/MAO system.

Homogeneous metallocene based catalysts are of theoretical significance in studies of Ziegler-Natta polymerization. Compared to conventional heterogeneous systems, in which a variety of active centers with different structures and activities

usually coexist, homogeneous catalysts give very uniform catalytically active sites, which possess controlled, well-defined ligand environments [28,29]. Therefore, the polymerization processes in homogeneous systems are often more simple, and kinetic and mechanistic analyses for these systems are greatly simplified. The recently developed base-free cationic metallocene is increasingly referred to as a "single-site" catalyst. The cationic metallocene catalyst affords a very simple and scientifically attractive system to investigate the details of stereoselective polymerization mechanisms.

N. Ishihara, M. Kuramoto, and M. Voi [30] found that a mixture of titanium compounds [$TiCl_4$, $Ti(OEt)_4$, or (η-C_5H_5)$TiCl_3$] with methylaluminoxane catalyzed the polymerization of styrene, even above room temperature, to the pure syndiotactic polystyrene, which had a narrow molecular weight distribution (Mw/Mn = 2). Pure syndiotactic polymers were also obtained with ring-substituted styrenes. Monomer reactivity was enhanced by electron-releasing substituents on the aromatic ring.

(η^5-Tetramethykcyclopentadienyl)-, (η^5-tetraphenylcyclopentadienyl)-, (η^5-(diphenylphosphino)tetramethylcyclopentadienyl)-, and (η^5-(trimethylsilyl) tetramethylcyclopenta-dienyl)titanium triisopropoxide have been synthesized and characterized by A. Kucht, H. Kucht et al. [31]. Their catalytic activities for syndiospecific styrene polymerization have been compared with the reference compound (η^5-cyclopentadienyl)titanium triisopropoxide, (η^5-tetramethyl cyclopentadienyl)titanium triisopropoxide was the best catalyst precursor, giving rise to catalysts having the highest activity to produce polystyrene with the highest syndiotactic yield and molecular weight.

J. C. Flores, J. C. W. Chien and M. D. Raush [32] discovered that {[2-(dimethylamino)ethyl]cyclopentadienyl}trichlorotitanium ($C_5H_4CH_2CH_2NMe_2$)-$TiCl_3$ has been prepared in 96% yield as a highly moisture-sensitive solid which was readily hydrolyzed to a μ-oxo derivative. The ^{1}H-NMR spectrum of ($C_5H_4CH_2CH_2NMe_2$)$TiCl_3$ was consistent with intramolecular coordination of the

dimethylamino group to titanium. $(C_5H_4CH_2CH_2NMe_2)TiCl_3$ compound exhibited relatively low activity as a styrene polymerization catalyst but is remarkably active for both ethylene and propylene polymerization.

P. Aaltonen and J. Seppala [33] studied the copolymerization of styrene and styrene for using the catalytic system $CpTiCl_3$-methyaluminoxane. The polymerization product was composed of polyethylene and syndiotactic polystyrene. No ethylene– styrene copolymer was detected. The composition of the product was dependent on the polymerization conditions. The catalyst activity was highest at polymerization temperature of 30^oC and Al/Ti ratio of 1500. Styrene content of the product was highest at polymerization temperature of 50^oC and Al/Ti ratio of 1500. The formation of separate polymer fractions might indicate a different polymerization mechanism for the two monomers, of the presence of more than one active species in the catalyst, one producing polyethylene and the other syndiotactic polystyrene.

K. Soga, T. Uozumi, et al. [34] investigated the catalyst of Cp_2ZrCl_2 and $[(C_5Me_4)SiMe_2N(t-Bu)]TiCl_2$ for polymerization of ethylene and copolymerization of ethylene with 1-octene and oligoethylene having a vinyl end group. The Cp_2ZrCl_2 catalyst combined with methyaluminoxane (MAO) gave polyethylene with vinyl, vinylidene and trans-vinylene groups. The use of $Al(iC_4H_9)_3$ or $(C_6H_5)_3C.B(C_6F_5)_4$ as cocatalyst produced polyethylene predominantly containing trans-vinylene groups. Polyethylene with vinyl end groups was obtained selectively with $[(C_5Me_4)SiMe_2N(t-Bu)]TiCl_2$-MAO as catalyst. The types and contents of $C=C$ double bonds in polyethylene markedly depend upon the metallocene compound as well as the cocatalyst. On the other hand, the $[(C_5Me_4)SiMe_2N(t-Bu)]TiCl_2$-MAO catalyst system for the copolymerizations gave poly[ethylene-co-(1-octene)] with a high content of 1-octene and a polyethylene containing an appreciable amount of long-side-chain oligoethylene.

Friedrich G. Sernetz, Rolf Mulhaupt [35] studied the influence of polymerization conditions on the copolymerization of styrene with ethylene using $Me_2Si(Me_4Cp)(N-tert-butyl)TiCl_2$/methyaluminoxane, respectively, in the monomer

feed lowered both activity of the catalyst system and molecular weight of the copolymer. Only at low styrene content, a linear correlation of styrene concentration in the monomer feed and styrene incorporation in the copolymer was found. From copolymerizations at various temperatures the activation energy of the insertion step was calculated to be 56 kJ/mol. Investigation of the thermal properties by means of differential scanning calorimetry and dynamic mechanical analysis revealed pronounced decrease of melting temperature and increase of glass transition temperature with increasing styrene content.

Claudio Pellecchia, Daniela Pappalardo, et al. [36] investigated the copolymerization of ethylene and styrene using the catalytic system η^5-C$_5$Me$_5$Ti(CH$_2$Ph)$_3$-B(C$_6$F$_3$)$_3$. Alternating ethylene-styrene copolymers was obtained, together with some polyethylene and syndiotactic polystyrene, from which the former could be seperated by solvent extraction. NMR analysis of suitably ^{13}C-enriched end groups shows that the regiospecificity of styrene insertion in the initiation step is largely secondary.

T. E. Ready, J. C. W. Chein, M. D. Rausch [37] discovered that a variety of 1- and 3-substituted alkylindines (R = H, Me, Et, tert-butyl, Me$_3$Si) as well as 2-methylindine have been prepared in good yields. The substituted indenes were converted into trimethylsilyl derivatives via reactions of intermediate organolithium complexes with chlorotrimethylsilane. The corresponding titanium complexes, (R- Ind)TiCl$_3$, were synthesized in excellent yield from reactions of the trimethylsilyl derivatives with TiCl$_4$. The titanium complexes were evaluated as styrene polymerization catalysts in toluene solution when activated by methylaluminoxane. Activities increased in the order: Cp< H$_4$Ind < Ind < 1-(Me)Ind < 2-(Me)Ind. A steep drop in activity was observed when R = Et, tert-butyl and Me$_3$Si, corresponding to an increase in the steric bulk of substituent in the catalyst precursor. 1-(Me$_3$S)IndTiCl$_3$ was found to be ineffective as a styrene polymerization catalyst. Syndiospecificities of the titanium complexes were generally very good (65-98%).

J. Sabmannshausen, et al. [38] discovered that mixtures of Cp*TiMe₃ and B(C_6F_5)₃ in mole ratios 1:1 was highly active for the polymerization of propene in toluene, light petroleum or liquid propene to give atactic polypropene of unusually high molecular weight (up to Mw = $4*10^{-6}$) and narrow dispersity. The polymer was elastomeric. The molecular weight distribution (M_w/M_n) revealed by Schulz-Zimm analysis of the GPC data was 1.1. The behavior of the catalyst indicated that a significant proportion of the titanium centers acted as living propene polymerization catalysts. Aluminium trialkyls were found to act as catalyst poisons, reducing polymer yield and molecular weight and substantially broadening the molecular weight distribution.

F. G. Sernetz, R. Mulhaupt and R. M. Waymouth [39] discovered that halfsandwich metallocene catalyst system Me₂Si(Me₄Cp)(N-tertbutyl)TiCl₂/MAO (Cp = cyclopentadienyl, Me = methyl, MAO = methylaluminoxane) gave homopolymers and copolymers of 1,5-hexadiene with ethene with high hexadiene content. According to ^{13}C-NMR spectroscopic microstructure analysis, cyclopolymerization of 1,5-hexadiene afforded randomly distributed cis- and trans-cyclopentane rings in the homo- and copolymer backbone. The ratio of vinyl side chains to cyclopentane rings was controlled by 1,5-hexadiene concentration, where low 1,5-hexadiene concentration promoted cyclopolymerization. Copolymer glass transition temperatures increased with increasing content of cyclic units in the backbone.

W. Kaminsky, et al. [40] investigated fluorinated half-sandwich complexes as catalysts in syndiospecific styrene polymerization. It was found that fluorinated half-sandwich complexes of titanium, such as CpTiF₃, showed an increase in activity of up to a factor of 50 compared to chlorinated compounds. In a temperature range of 10-70°C the methyaluminoxane (MAO) could be reduced to an Al:Ti ratio of 300. If the cyclopentadienyl ligand in the metallocene is changed to a pentamethylcyclopentadienyl ligand (Cp*) which is a stronger electron donor and exerts a greater sterical hindrance, the polymerization activity is lowered. But the

pentamethylcyclopentadienyltitanium fluoride (Cp*TiF$_3$) could be produced the polystyrene with highest melting point of 277°C.

Friedrich G. Sernetz, et al. [41] studied the copolymerization of ethene with styrene. Ethene was copolymerized with styrene using five different methylaluminoxane (MAO) activated half-sandwich complexes of the general formular Me$_2$Si(Cp)(N-R)MCl$_2$, varying the substituents on the cyclopentadienyl ring and the substituent on the amide (Cp = tetramethylcyclopentadiene CBT, 1-indenyl IBT, 3-trimethylsilyl-1-indenyl SIBT, or fluorenyl FBZ; R = tert-butyl (complexes CBT, IBT, SIBT, FBZ) or benzyl CAT), as well as the metal center (M = Ti, except FBZ:M = Zr). All complexes produced random poly(ethene-co-styrene) without any regioregular or stereoregular microstructure. Complex CBT showed the highest catalytic activity, the fluorenyl substituted complex FBZ produced the highest molecular weight polymer and complexes SIBT and CAT promoted high styrene incorporation. Bulky substituents on the Cp-ligand resulted in steric hindrance, thus reducing styrene incorporation but increasing long-term activity of the catalyst during the polymerization. Moreover, deactivation was accelerated with increasing styrene concentration. ^{13}C-NMR spectroscopic microstructure analysis showed exclusively tail-to-tail coupling of styrene units in the polymer backbone.

Qing Wu, Zhong Ye, Shangan Lin [42] investigated syndiotactic polymerization of styrene with cyclopentadienyltribenzyloxytitanium/ methylaluminoxane [MAO] catalyst. The reaction conditions, e.g., [Ti], [MAO], [St], temperature and the content of retained trimethylaluminium (TMA) in MAO effected on the catalytic activity, syndiotacticity and molecular weight of the polymer. With [MAO] = 0.17mol/l, the catalyst exhibits higher activites. The catalytic activity increased with increase of [MAO], and reaches a maximum value at [MAO] of 0.5 mol/l. The molecular weight of the polymer decreased and the molecular weight distribution became narrow with increasing the [MAO]. The [MAO] was necessary for activating the titanocene molecules and scavenging of impurities. Additionally, the MAO acted as a chain transfer agent, so that the higher the [MAO] used, the lower

is the molecular weight of the polystyrene produced. The catalytic activity was directly proportional to the monomer concentration.

A variety of methoxy-substituted(indenyl)trichlorotitanium complexes [(η^5-(2-methoxyethyl)cyclopentadienyl)trichlorotitanium, (η^5-1-(2-methoxyethyl) indenyl)trichlorotitanium, (η^5-1-(2-methoxyphenyl)indenyl)trichlorotitanium] were synthesized by P. Foster, M. O. Raush and J. C. W. Chein [43]. These precusors were used to polymerize styrene, ethylene and propylene. The complexes, when activated with methylaluminoxane (MAO), show only low activity for d-olefin polymerization. Since MAO was a polymeric species, when oxygen-aluminum coordination took place the amount of steric hindrance around the catalytic center is dramatically increased, which could inhibit monomer coordination.

Furthermore, the oxygen-aluminum coordination could substantially decrease the ability of MAO to abstract an anionic ligand from titanium to form the cationic organotitanium active species.

Y. Kim, B. H. Koo, Y. Do [44] synthesized and characterized five substituted indenyltrichlorotitanium compounds with spectroscopic methods. Their catalytic behavior for the polymerization of styrene was studied in the presence of methylaluminoxane (MAO) as a cocatalyst. Substituted indenyl ligands include 1,3-dimethyl, 1-methyl, 1-ethyl, 1-isopropyl and 1-(trimethylsilyl)indenyl groups. All five compounds gave extremely pure syndiotactic polystyrene and conversion rates of at least 95%. The UV-visible and $^{47, 49}$Ti NMR Spectra provided a consistent measure of the electron densities at the metal centers of five substituted indenyltrichlorotitanium compounds. The catalytic activity was enhanced by less bulky and better electron-releasing substituents of the indenyl ligand.

Cyclopenta[1]phenanthrene titanium trichloride and its 2-methyl and phenyl derivatives were synthesized by N. Schneider, M. H. Prosene, and H. H. Brintzinger [45]. The crystal structure of the 2-methyl-substituted complex was determined by X-ray diffraction analysis. In the presence of methylaluminoxane (MAO), these

complexes give highly active catalysts for the syndiotactic polymerization of styrene. The 2-phenyl-substituted complex exceeded all previously described catalysts in its catalytic activity.

T. Arai, T. Ohtsu and S. Suzuhi [46] found that the catalyst system of rac-[isopropylidenebis(1-indenyl)]zirconium dichloride and MAO could be produced a stereoregular and Bernoullian copolymer of styrene and ethylene. This catalyst gave a high molecular weight copolymer with good activity at 50°C. The copolymer consists of Ethylene (Et)-Et, Styrene (St)-Et and head to tail St-St sequences and has a highly isotactic Et-St alternating sequence. This copolymer showed a melting point (80-110°C) due to the isotactic alternating sequence.

Qing Wu, Zhong Ye, Qinghai Gao and Shangan Lin [47] found that mono(η^5-cyclopentadienyl)titanium tribenzyloxide activated with methylaluminoxane (MAO) could be polymerized propylene. The content of residual trimethylaluminium (TMA) in MAO had a determinative effect on the polymerization. An excess of TMA in the catalyst system reduced the Ti species to inactive lower valence states. The catalyst system gives medium molecular-weight atactic polypropylene ($M_v = 2\text{-}7*10^4$) with narrow molecular weight distribution ($M_w/M_n = 1.4\text{-}1.8$). The catalyst system exhibited high activities in the temperature range of 40-50°C. The optimum molar ratio of MAO to the titanocene for the polymerization is approximately 150. Raising the Al/Ti ratio caused an obvious decrease of the catalytic activity.

(η^5-trimethylsiloxytetramethylcyclopentadienyl) and (η^5-2-trimethylsiloxy indenyl) trichlorotitanium have been synthesized and characterized by G. Tian, S. Xu, Y. Zhang, B. Wang and X. Zhou [48]. Their catalytic behavior for the polymerization of styrene was studied in the presence of methylaluminoxane (MAO) as a cocatalyst. The cocatalyst MAO, as a lewis-acid, might coordinate with oxygen atom of siloxy group. The coordination suppressed the resonance effect and enhances the inductive effect of the siloxy group. As a result, the compounds showed only low activity for styrene polymerization.