Chapter 1. Introduction

1.1. Polyolefins

Polyolefins form a highly important class of materials, with a wide range of applications, which are produced industrially on a huge scale (> 85 Mton per year). By far the largest volume of these polyolefins is linear polyethylene (HDPE) and its copolymers with 1-alkenes (LLDPE), and isotactic polypropene (iPP). These polymers are all prepared by the catalytic (co-)polymerization of olefins using transition-metal catalysts. As polyethenes and polypropenes consist essentially of very long alkane molecules, these materials are very apolar and lipophilic. Although polyolefins serve a wide range of applications, their apolar nature limits their properties in certain areas, e.g. with respect to its barrier properties and permeability, dyeability, printability, and compatibility with more polar materials (such as glass fiber for reinforcement). It therefore would be desirable for certain applications to modify the polymer by introducing polar functional groups, with retention of the other favorable properties, like modulus, strength, solvent resistance, etc. \(^{1,2}\)

The conceptually most straightforward method to introduce polar functionalities into polyolefin materials is the incorporation into the polymer of comonomers with polar functional groups, such as alcohol, ester or amine functionalities. Once a copolymer bearing functionalities is obtained, further chemical derivatization using these reactive groups would be possible. Presently, the commercial copolymerization of ethene with polar monomers is only carried out in high pressure radical polymerization processes, used to generate highly branched low-density polyethene (LDPE).\(^{3,4,5}\)
The metal-catalyzed copolymerization of simple alkenes, like ethene and propene, with functionalized olefin comonomers has to contend with certain inherent difficulties, which are related to the fundamentals of the catalyzed polymerization process. Transition-metal catalyzed olefin polymerization proceeds on metal alkyl species via a reaction sequence known as the Cossee-Arlman mechanism (Scheme 1.1). An electron-deficient metal alkyl species, with a vacant coordination site, can bind a molecule of olefin monomer, which then undergoes a migratory insertion reaction in which a new carbon-carbon bond is formed, and the vacant site is regenerated.

When a comonomer contains a polar functionality, this usually is Lewis basic, and will compete for binding to the Lewis acidic catalyst metal center with the olefinic group. If this binding is reversible, it will in the best cases still lead to a certain catalyst inhibition, slowing down the catalysis. This inhibition can be significantly enhanced after insertion of the functionalized comonomer into the metal-carbon bond, when there is a possibility for intramolecular coordination of the functionality to the metal center. Chelate complexes thus formed can be very stable, and lead to a further decrease in catalyst performance. In addition, many polar functionalities react in an irreversible way with the polarized metal-alkyl bond. Protic functionalities like alcohols will protonate the alkyl group, destroying the metal-carbon bond that is essential for the polymerization catalysis. Carbonyl functionalities in aldehyde or ester groups are susceptible to nucleophilic attack by the alkyl group bound to the metal, especially when the metal is
relatively electropositive. In each of these cases, irreversible, and often rapid, catalyst deactivation will result (Scheme 1.2). It is therefore clear that the catalytic copolymerization of ethene or propene with functional comonomers is by no means an easy undertaking.

Scheme 1.2

In recent years, considerable effort has been directed to finding strategies for incorporation functional comonomers into polyolefins by catalytic copolymerization.\(^6\)\(^,\)\(^7\)\(^,\)\(^8\) In the next paragraphs, a brief survey is given of several approaches taken to this end. For further development in this area, an increased understanding of the strength and nature of the interactions between these functional comonomers and various catalyst types is desirable. The work described in this thesis seeks to contribute to this understanding.
1.2. Early transition metal catalysts

Since the discoveries by Ziegler and Natta that ethene and propene can be effectively polymerized by heterogeneous catalysts generated from combinations of titanium halides and alkyl aluminum compounds, this group 4 metal has been the mainstay of industrial polyolefin production. The subsequent development of soluble, well-defined (“single site”) organometallic olefin polymerization catalysts also focused initially on the group 4 metals, especially titanium and zirconium. As these metals are electropositive, hard Lewis acidic and “oxophilic” (i.e. with M-O bonds being considerably stronger than M-C bonds), they are not easily applied to copolymerizations involving heteroatom-containing comonomers.

Many strategies were developed to avoid these problems. The most applied in copolymerizations of functionalized comonomers with early transition metal catalysts is the functional group protection strategy. The polar functionalities are protected by incorporating very high levels of Lewis acids, e.g. AlCl₃, tetramethylaluminium (TMA) into the copolymerization system to weaken or prevent the strong interactions between the catalysts and the functionalities. For example, comonomers with -OH groups were reacted with an excess of Al-alkyl to generate protected functionalities -OAlR₂. The -OH functionality was regenerated upon hydrolytic work-up after polymerization.

A related strategy uses comonomers in which the functionalities are already protected by hydrolysable groups e.g. -OSiR₃ and -N(SiMe₃)₂. Upon hydrolytic work-up after the polymerization, –OH or –NH₂ functionalities are generated on the polymer.

The introduction of sterically demanding groups on a heteroatom in the functionalized comonomer can be sufficient to disfavor metal-functionality interactions interfering with the polymerization process. An example is 5-(N,N-diisopropylamino)-1-pentene, which is readily copolymerized
with olefins. Unfavorable interactions of a polar group with the catalyst metal center can also be decreased when the functional group on the monomer is located far away from the double bond (separated from it by a spacer group). This disfavors the formation of stable chelates by intramolecular interaction after insertion of the comonomer. This ‘spacer strategy’ is more effective when it is combined with other ‘protection strategies’ that diminish intermolecular metal-functionality interactions, e.g. in the copolymerization of 10-undecene derivatives.\textsuperscript{26,27}

Alternative routes to functionalized polyolefin copolymers have been devised that avoid the use of insertion polymerization catalysis. Examples are the catalytic ring-opening metathesis polymerization (ROMP) of cyclic olefins and functionalization of the resulting unsaturated polymer, and catalytic ROMP of cycloolefins bearing polar functionalities (metathesis catalysts generally being more resistant to polar functionalities than catalysts for insertion polymerization), followed by hydrogenation to remove the remaining unsaturation in the polymer backbone.\textsuperscript{28,29}

### 1.3. Late transition metal catalysts

Compared with early transition metal catalysts, the less electropositive, softer Lewis acidic nature and lower oxophilicity of the later transition metal complexes generally lead to a greater functional-group tolerance.\textsuperscript{30,7} Nevertheless, late transition-metals have only relatively recently been successfully applied in the catalytic synthesis of high polymer polyolefins. The reason for this is that, for these metals, chain transfer processes are relatively facile, leading to the formation of low molecular-weight products (Scheme 1.3).\textsuperscript{31,32}
Many efforts have been made on finding proper ligands for late transition metal complexes to prevent $\beta$-H elimination to achieve a polymerization. Sterically demanding $\alpha$-diimine ligands are successful examples of ligands that can diminish the rate of chain-transfer relative to that of chain growth due to their steric hindrance. A number of well-defined catalysts based on complexes of iron and cobalt, rhodium and platinum, nickel and palladium, etc. were reported to be able to polymerize olefins to high polymers with reasonable activities. However, only few of them show an appreciable ability to incorporation of polar olefins.  

The various approaches taken with late transition-metal catalysts to copolymerize ethene with functionalized comonomers will be outlined in following sections.

Many late transition-metal catalysts (but especially the ones based on palladium) display a peculiar behavior called “chain-walking”. Through sequential $\beta$-H elimination, olefin rotation and olefin re-insertion steps (Scheme 1.4), the metal center can “walk” along the carbon chain of the polymer. The result of this behavior is that these catalysts can homopolymerize ethene to branched polyethene, but also that the “spacer strategy”, mentioned in section 1.2, is ineffective: even when the olefinic moiety and the polar functionality in the comonomer are separated by a -(CH$_2$)$_n$- spacer, the metal center can “walk” along that chain to the functionality, to form the most stable (and therefore least reactive) chelate complex.
A way to counter this problem is to place a quaternary center between the olefinic group and the functional group in the comonomer, which will prevent the catalyst from walking all the way up to the functionality. Copolymerizations of ethene with diethyl allylmalonate and methyl 2,2-dimethyl-4-pentenoate are examples of this blocked chain strategy. 

1.4. Cationic Pd and Ni α-diimine catalysts

The cationic α-diimine Ni and Pd catalysts [(N\textsuperscript{N})ML][BAF] (Scheme 1.5) were first reported by Brookhart and co-workers in 1995.\textsuperscript{37} By applying a bulky α-diimine ligand around the metal center to prevent chain-transfer, the catalysts can successfully catalyze homopolymerization of ethene, α-olefins and internal olefins to high molecular weight polymers. This type
of catalysts is ready to take chain-walking so the products are highly branched polymers, varying from semi-crystalline to amorphous. 43,44

The high tolerance of these catalysts to functionalized comonomers generated a lot of research interest. Ethene polymerizations can be carried out in the presence of ethers, organic esters, and acids. 45,46 And this functional-group tolerance extends to comonomers bearing polar functionality, e.g. acrylates. The copolymerizations of ethene and propene with acrylates in an unprotected form to give high molecular weight and random copolymers were reported by Brookhart and co-workers. 39,47 This was really the first successful attempt to copolymerization of conventional polar comonomers, although the rate of incorporation of acrylates is still rather low. 48, 49, 50 Similar to corresponding ethene homopolymers synthesized with these catalysts, the copolymers are highly branched (~100 branches/1000 carbon atoms) and the ester groups are located predominantly at the ends of branches. 51, 52 Details of this particular copolymerization will be illustrated in Chapter 3.

The success of copolymerizations of ethene and propene with acrylates encourages more attempts to copolymerize other functionalized comonomers using α-diimine Ni or Pd catalysts. Combining the ‘spacer strategy’ and protection with trimethylaluminum, 5-hexen-1-ol, 10-undecen-1-oic acid etc. were copolymerized with ethene or propene by α-diimine nickel catalysts. 53 DuPont researchers claimed the copolymerization of a range of polar monomers, e.g. fluoro-functionalized comonomers (CH$_2$=CH(CH$_2$)$_3$C(CF$_3$)$_3$, etc.), chlorosilanes (CH$_2$=CH(CH$_2$)$_6$SiCl$_3$, etc.) and siloxanes (CH$_2$=CHSi(OR)$_3$, etc.) with ethene by using these catalysts. The copolymers with silane functionality can be cross-linked by hydrolysis, e.g. when they are exposed to moist air. 54, 55, 56, 57 However, some polar monomers were found to inhibit polymerization completely, e.g. vinyl acetate, acrylamide and acrylonitrile. 7
1.5. Neutral Pd(II) and Ni(II)-based catalysts

Neutral nickel hydride complexes bearing monoanionic phosphine-alkoxide chelating ligands are well-known catalysts for SHOP (Shell Higher Olefin Process): the catalytic oligomerization of ethene to linear 1-alkenes. Apparently, the chain-transfer reaction competes with the chain-growth process to lead to oligomers. In order to achieve a polymerization, the steric demand strategy which was succeeded in the cationic α-diimine systems was extended to the neutral nickel catalysts. A series of salicylaldimine ligands with bulky aryl substituents lying adjacent to the phenoxide substituent were selected for the new nickel catalysts (Scheme 1.6) to polymerize ethene or propene to high molecular weights and highly linear polymers even in the presence of ethers, ketones, esters, alcohols, amines and water.\(^{58, 59, 60}\) Furthermore, copolymerizations of ethene with functionalized norbornenes such as 5-norbornen-2-ol and 5-norbornene-2-yl acetate were reported by Grubbs and co-workers.\(^{61}\) However, attempts to copolymerize functionalized vinyl monomers and ethene were not succeeded. A deactivation mechanism involving hydrogen transfer from substrate to Ni complex was found in a reaction of the catalyst and deuterated methyl acrylate.\(^{62}\)

![Scheme 1.6](image-url)

\[ L = \text{Ph}_3\text{P}, \text{CH}_3\text{CN} \]
\[ R = \text{H}, \text{Ph}, \text{9-antheracene} \]
\[ R' = \text{Ph}, \text{CH}_3, \text{etc.} \]
Neutral palladium complexes are the most recently studied catalyst family for the copolymerization of ethene with functional vinyl monomers. An early study by Drent and co-workers revealed the incorporation of methyl acrylate (MA) into linear polyethene using a neutral palladium catalyst with a chelating P-O (di(2-methoxyphenyl)phosphinobenzene-2-sulfonate) ligand. Random copolymers of ethene and acrylate (2-17 mol%) with modest molecular weight ($M_n = 2,000 – 20,000$) was obtained.\textsuperscript{63} Another neutral palladium catalyst, (PO-OMe)PdMe(pyridine) (PO-OMe: 2-[bis(2-methoxyphenyl)phosphino]-4-methyl-benzenesulfonate), was reported very recently to copolymerize ethene and alkyl vinyl ethers to linear polymers with in-chain and chain-end functional groups.\textsuperscript{64} At same time, this catalyst was also applied in copolymerization of ethene and acrylonitrile to yield similar polymer.\textsuperscript{65}

1.6. Research objectives and survey of the thesis

As mentioned above, Pd $\alpha$-diimine catalysts have shown considerable promise in the copolymerization of functionalized olefins with ethene. Nevertheless, most of the attention in this area has focused on monomers of direct commercial interest (methyl acrylate, acrylonitrile). These catalysts also provide a good platform for systematic studies that can give more fundamental information on the substrate-catalyst interactions of a wide range of substrates. This information can be useful for future endeavors in the search for new functional polyolefin materials.

In this thesis the interactions between the cationic $\alpha$-diimine palladium catalyst [$(N^N)\text{PdMe(OEt}_2)]\text{[BAF]}$ (2, $N^N$: $\text{ArN=CMe-CMe=NAr}$ with $\text{Ar}$: 2,6-diisopropylphenyl, $\text{BAF}$: $\text{B}[3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3]_4$) and heteroatom-containing monomers with different functional groups (ether, amine, thioether etc.) were studied. Copolymerizations of ethene with these functionalized comonomers were also explored.
In Chapter 2, the synthesis of the cationic α-diimine palladium catalyst 2 is revisited. A new, convenient synthesis of the catalyst precursor \((N^N)\text{PdMe}_2\) (1) is presented. It turns out that the details of the reaction conditions are important in the generation of the ionic complex 2. A side product in the reaction was identified as the \(\mu\)-methyl, \(\mu\)-methylene complex \(\{\text{(N}^\text{N})\text{Pd(µ-CH}_3)(µ-\text{CH}_2)\text{Pd(N}^\text{N})\}\)[BAF] (3). The compound is formed by reaction of 2 with the starting material 1. The molecular and electronic structure of 3 and some of its reactivity features were explored.

Chapter 3 describes the reaction of the cationic Pd-catalyst 2 with olefins bearing oxygen-containing functionalities: acrolein dimethyl acetal (ADMA), allyl ethyl ether (AEE) and 2-vinyl-1,3-dioxolane (VDO). AEE and ADMA smoothly give 1,2-insertion into the Pd-Me bond of 2 to give the 5-membered chelate complexes \([(N^N)\text{Pd(CH}_2\text{CHMeCH}_2\text{OEt})]\)[BAF] (9) and \{\text{(N}^\text{N})\text{Pd}[\text{CH}_2\text{CHMeCH(OMe)}_2]\}[BAF] (11) respectively. Both are able to catalyze the homopolymerization of ethene. Attempted ethene/AEE copolymerization resulted in rapid catalyst deactivation, forming the allyl complex \([(N^N)\text{Pd}(\eta^3-1-\text{CH}_2\text{CHCH}_2)]\)[BAF] (10) and ethanol. Nevertheless, the ethene/ADMA copolymerization successfully yielded a branched polyethylene copolymer bearing acetal functionalities. Here too, gradual deactivation takes place through formation of an allylic complex, \([(N^N)\text{Pd}(\eta^3-1-\text{CH}_2\text{CHCHOMe})]\)[BAF] (12), and methanol. This deactivation could be retarded by the addition of aliquots of methanol to the reaction mixture. In contrast, VDO very readily ring-opens in the presence of 2, and could not be copolymerized.

Chapter 4 describes the reaction of the cationic Pd-catalyst 2 with olefins bearing nitrogen-containing functionalities: allyl dimethyl amine (ADA), N-allyl carbazole (NAC) and 5-pentenyl carbazole (NPC). ADA reacts with 2 via smooth 1,2-insertion to give the 5-membered chelate complex \([(N^N)\text{Pd(CH}_2\text{CHMeCH}_2\text{NMe}_2)]\)[BAF] (14). In contrast to the ether chelates from chapter 3, this compound does not catalyze the homopolymerization of ethene, due to the stronger Lewis basicity of the
amine. NAC and NPC react with 2 to form unusual 3-membered chelate complexes after insertion into the Pd-Me bond and “chain-walking”. The product from NPC, \((N^N)\text{Pd}[\text{Me}_2\text{CHC}_2\text{H}_4\text{CHN(C}_6\text{H}_4\text{)}_2]\)[BAF] (15), was structurally characterized. These 3-membered chelates readily react with ethene, and NPC was successfully copolymerized with ethene to give branched polyethene copolymers bearing carbazole functionalities. The fluorescence of the carbazole group in these copolymers is highly dependent on the comonomer content. In contrast to NPC, NAC is not incorporated upon attempted copolymerization, probably due to the steric hindrance imparted by the carbazole group close to the olefinic moiety.

Chapter 5 describes the reaction of the cationic Pd-catalyst 2 with olefins bearing sulfur-containing functionalities: allyl methyl thioether (AMT), allyl tert-butyl thioether (ABT), 2-allyl-1,3-dithiane (ADT) and 2-pentenyl-2-methyl-1,3-dithiane (PMDT). AMT reacts with 2 to give the stable thioether adduct \((N^N)\text{PdMe(κ1-MeSCH}_2\text{CH=CH}_2)]\)[BAF] (17): the soft Lewis basic thioether effectively competes with the olefinic moiety for coordination with the metal, blocking insertion into the Pd-Me bond. The substrates ABT and PMDT, where the S-atoms are more screened by steric hindrance, do insert into the Pd-Me bond to give 5-membered chelates, which were structurally characterized. Nevertheless, due to the strong intramolecular Pd-S interactions in these complexes, reactivity with ethene (and thus the possibility for copolymerization) is impeded.

1.7. References


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