Polyolefins

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Post-Metallocenes in the Industrial Production of Polyolefins

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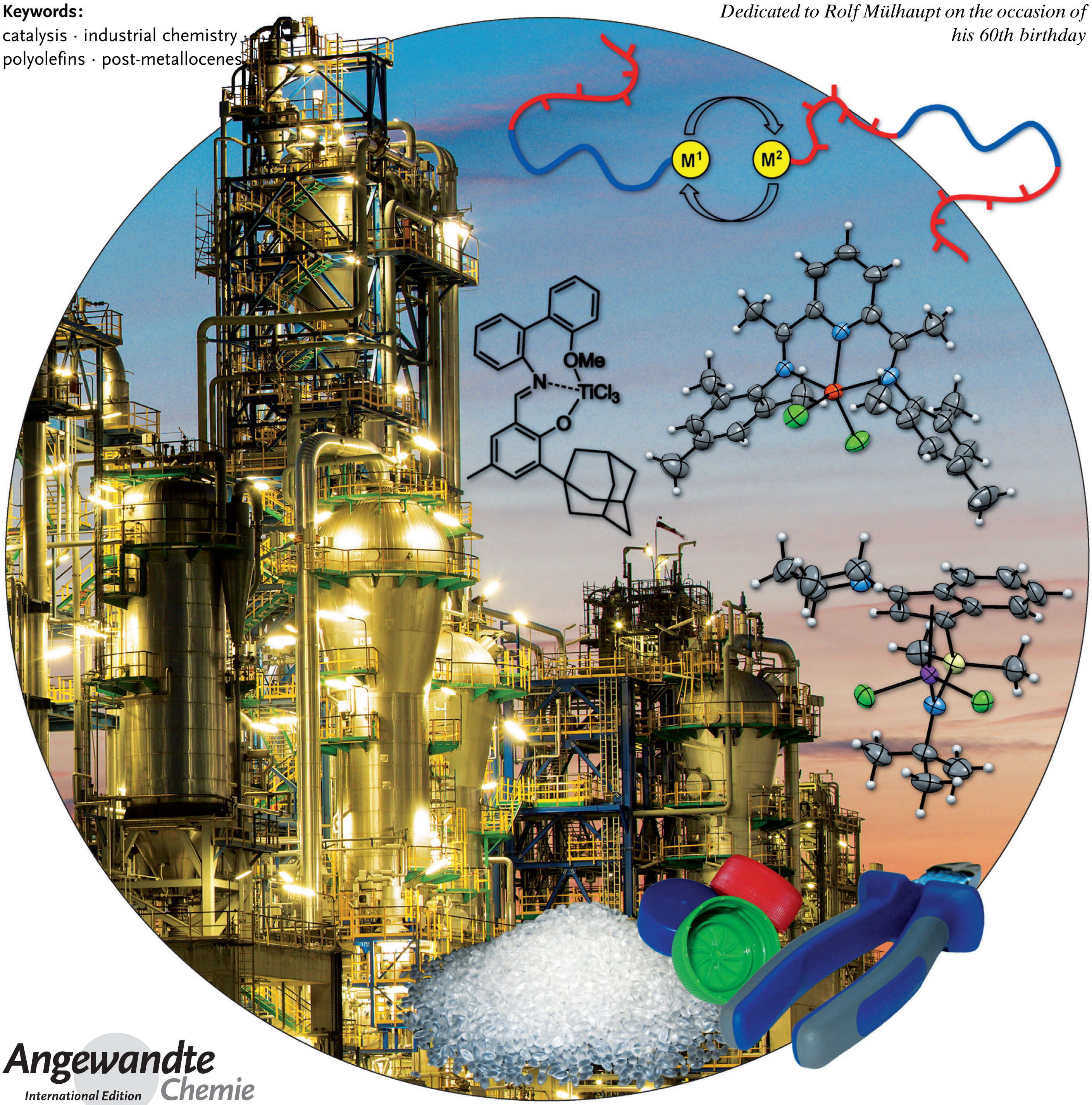
Dedicated to Rolf Mülhaupt on the occasion of his 60th birthday



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Research on "post-metallocene" polymerization catalysis ranges methodologically from fundamental mechanistic studies of polymerization reactions over catalyst design to material properties of the polyolefins prepared. A common goal of these studies is the creation of practically useful new polyolefin materials or polymerization processes. This Review gives a comprehensive overview of post-metallocene polymerization catalysts that have been put into practice. The decisive properties for this success of a given catalyst structure are delineated.

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1. Introduction

Catalytic insertion polymerization of olefins is one of the most widely studied synthetic reactions. In terms of a mechanistic understanding and a rational design of catalysts, the finding that *ansa*-metallocenes can allow for a control of polypropylene tacticity in the 1980s marked a milestone.[1] This sparked intense research by numerous academic and industrial laboratories in metallocene catalysts.[2] In the 1990s, this interest expanded to catalysis by well-defined metal complexes with other ligand motifs, also summarized as "post-metallocenes". An early prominent example was provided by half-sandwich cyclopentadienyl–amide titanium catalysts for ethylene/1-olefin copolymerization. This development was further augmented by findings of cationic late-transition-metal olefin polymerization catalysts. Consequently, a large scope of coordination compounds and organometallic species across the periodic table were studied. The breadth of these investigations was documented by comprehensive reviews in this and other journals.[3–6] Within this realm, even the more fundamental studies of coordination chemistry and mechanisms were obviously performed before the background of finding catalysts for improved processes or the generation of enhanced polyolefin materials. The question then arises as to how these developments have actually succeeded in practice. A comprehensive overview is given of catalyst systems employed industrially, including underlying fundamental organometallic and coordination properties relevant to their utilizations.

In 2009, polyolefin production was a 110 million tons per year market. This breaks down into 44 million tons per year of polypropylenes (PP) and 67 million tons per year of polyethylenes (PE), including HDPE, LLDPE, and LDPE (HD = high density, LLD = linear low density, LD = low density).[7] Apart from LDPE, which is prepared by radical polymerization at high pressure and temperature, all of these polymers are produced by catalytic olefin insertion polymerization. This is one of the largest industrial applications of catalysis. Mostly these polymers are produced by Ziegler–Natta catalysis with heterogeneous multi-site catalysts generated from simple titanium compounds, such as $TiCl_4$, activators, donors, and a support such as $MgCl_2$, but there is also a growing market for single-site polyolefins, which exhibit more defined microstructures, controlled molecular weight distributions, and superior mechanical properties and clarity. In 2009, a quarter (ca. 5 mio tons) of the worldwide LLDPE production was based on single-site catalysts. Another 3 million tons of HDPE and ca. 1 million tons of PP resins were produced by single-site catalyst technology.[8] These single-site catalysts are often metallocenes, but during the last two decades an increasing number of polymerization processes employing post- or non-metallocene catalysts have been commercialized. Obviously, different companies disclose the technical details and the status of their applied technologies to a greater or lesser extent, leaving room for interpretation in some cases.

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2. Activators

Just like metallocene catalysts, most industrially relevant post-metallocene catalysts require an activator to generate the catalytically active center.[4,9] Although post-metallocene catalysts in itself consist of many different catalyst families, the activators (that is, co-catalysts) are in fact the same as used for the metallocene catalysts; thus the development of new activators does not seem to target specific classes of (post-) metallocene catalysts. The well-known activators which were developed until the 1990s that are still used and are readily available from commercial suppliers include the aluminoxanes (methylaluminoxanes (MAO) and modified methylaluminoxanes, which contain higher alkyl groups (MMAO)), tris(pentafluorophenyl)borane and the tetrakis(pentafluorophenyl)borate based ion pairs, which commonly contain triphenylcarbenium or ammonium (for example, $PhNHMe_2^+$) cations.[9]

For solution polymerization, these activators are preferably soluble in apolar solvents, such as Isopar E and hexanes. Whereas hexane-soluble modified methylaluminoxanes (MMAO) and tris(pentafluorophenyl)borane can be used, generally the most productive catalyst systems usually are obtained by using the ionic tetrakis(pentafluorophenyl)borates; however, these are insoluble in such apolar solvents. Therefore efforts were made to make these ion pairs soluble by introducing aliphatic chains on the cation. Exxon filed patents on introducing alkylsilane groups on the triphenyl carbenium part,[10] whereas Dow introduced longer alkyl chains on the quarternary ammonium cation (for example, $(C_{18}H_{37})_2NHMe^+$) using commercially available amines.[11]

However, some industrial applications of single-site catalysts are not in solution-phase olefin polymerization, but in gas-phase and slurry-phase polymerization. The method to support these single-site catalysts commonly involves the addition of the catalyst precursor to metal oxide supports (in particular silica supports). Exxon described the synthesis of silica-supported borate anions from the reaction of silica with tris(pentafluorophenyl)borane in the presence of a base.[12] Dow and W. R. Grace have described how borate co-catalysts can be tethered to a partially dehydroxylated or an aluminum alkyl treated silica support. This is performed by employing a borate anion that forms a chemical bond to the silica surface,[13] which is a very elegant procedure to support many different metallocenes and non-metallocenes, such as the Dow constrained geometry catalyst. More recently, Albemarle filed a method, in analogy to the ionic dimethylanilinium tetrakis(pentafluorophenyl)borate used for solution polymerization, to make a silica-supported Brønsted acidic activator through modification of a silica support, which had previously been treated with excess triethylaluminum, with a Lewis base, such as dimethylaniline, and subsequently with pentafluorophenol.[14] This method was claimed to result in high catalyst productivity and no reactor fouling.

Aluminoxane-based polymerization catalyst activators still serve as the workhorse in many commercial applications of single-site catalysts despite the disadvantages they have, such as their high aluminum-to-metal ratios owing to the low activation efficiency and the catalyst poisoning effect the non-hydrolyzed aluminum alkyls have. The reason for that is that aluminoxane-based catalyst systems still have some other benefits over alternative activator systems, such as being capable of (though low efficient; see above) in situ metal alkylation, its ability to scavenge catalyst poisons, the ease by which catalyst precursors can be supported onto an aluminoxane containing carrier, and the lower catalyst decomposition rates that many single-site catalysts have when they are activated by aluminoxanes,[15,16] although this is not a very general statement to be made, as it will be very much residence-time- and catalyst-precursor-dependent.[17] Notable efforts have been made in more recent years to improve aluminoxane activator efficiency by attempting to promote the formation of dialkylaluminum cations. These dialkylaluminum cations in the alkylaluminoxanes are believed to be the actual activating components,[18,19] which lead to the formation of the fully alkylated stable chelated cationic bimetallic (mixed Group 4/aluminum) complexes (Figure 1).[20,21] An example of an X-ray crystallographic determination for the existence of such structures was presented for a non-metallocene cation of this type by Mountford et al.[22]

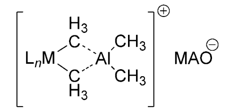


Figure 1. Structure of aluminum-chelated cationic catalyst species.

Ionic methylaluminoxane was isolated by treating a regular commercial

Moritz Baier studied Chemistry at the University of Konstanz. He obtained his M.Sc. in Chemistry in 2009 under the supervision of S. Mecking. Currently he is in the final stages of his Ph.D. studies on living insertion polymerization for the synthesis of well-defined dye-labeled polyolefins and the preparation of ultrahigh-molecular-weight polyethylenes in the group of S. Mecking. For these studies he received a Chemiefonds scholarship of the Fonds der Chemischen Industrie.

Martin Zuideveld received his Ph.D. degree from the University of Amsterdam under the guidance of P. W. N. M. van Leeuwen in 2001. After a two-year postdoctoral stay in the group of S. Mecking in Freiburg as an Alexander von Humboldt Fellow, he joined DSM Research B.V. in Geleen, The Netherlands, in 2003. In 2009, he became group leader of the Advanced Catalysis and Explorative Research group of DSM Elastomers B.V., which was acquired by Lanxess AG in 2011. Since March 2012, he has been working as a Staff Scientist on Medium and High Throughput Polyolefin research at SABIC's Science and Technology Center in Geleen, The Netherlands.

MAO with octamethyltrisiloxane (OMTS).[23] The addition of OMTS to a 30 wt % solution of methylaluminoxane in toluene leads to the formation of two separate phases of which the ionic phase consists of $[(Me_2Al{\cdot}OMTS)^+(MAO\text{-}Me)^-]$. The isolated ionic phase possessed a much higher activation efficiency. As this method is obviously not commercially attractive, which is due to the non-ionic phase of the treated MAO not being used, other methods were explored to enhance the number of dimethylaluminum cations in MAO. This resulted in the finding of so-called dimethylaluminum cation precursor agents, which could enhance the number of dimethylaluminum cations in MAO.[24] For silica supported complexes, it was shown that the number of dimethylaluminum cations could be increased by treating SiO_2-supported MAO with dimethylaluminum fluoride. NMR experiments showed that catalyst precursors were more readily activated by the silica supported MAO treated with dimethylaluminum fluoride. Most recently, methods were described to make supported single-site catalysts using a carbocationic agent, such as α,α,α-trifluorotoluene, giving more productive catalysts that are claimed not to give reactor fouling.[25]

Instead of increasing the activation efficiency of an alkylaluminoxane (or rather in conjunction), another approach to enhance the productivity of MAO activated olefin polymerization is to obtain a more productive catalyst by reducing the catalyst inhibiting effect that the residual trimethylaluminum (TMA) in MAO has. Busico et al. and Collins et al. described that the addition of a sterically hindered phenol, such as 2,6-di-*tert*-buyl-4-methylphenol (BHT), to an MAO activated system enhances the productivity of such a catalytic system.[26,27] This effect was also described in patents filed by Mitsui.[28] Busico reported that the TMA is able to coordinate to the cationic M-alkyl complex and therefore, yields a less productive catalyst. Further, side reactions of a fluorinated phenoxyimine titanium complex with TMA, which lead to a less controlled polymerization behavior, can be eliminated by the addition of BHT. Collins et al. described why exactly a sterically demanding phenol such as BHT should be used, as BHT reacts instantaneously with trimethylaluminum and only very slowly with the M-alkyl bond of the transition-metal cation.[29]

Stephan et al. described that the ethylene polymerization activity of the non-metallocene $[CpTiMe_2(NPtBu_3)]/B(C_6F_5)_3$ increased upon the addition of bulky phosphines, such as $PtBu_3$, to the catalyst system.[30] They suggest that the phosphine, though not being able to form a dative Ti−P bond, does alter the environment of the active site and facilitates the cation–anion separation.

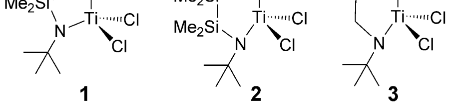
Stefan Mecking received his Ph.D. degree from RWTH Aachen under the guidance of W. Keim in 1994. After a postdoctoral stay in the group of M. Brookhart (University of North Carolina at Chapel Hill) as a Feodor Lynen Fellow of the Alexander von Humboldt Foundation, he joined the corporate research of Hoechst AG in Frankfurt. In 1998 he joined Freiburg University, where he habilitated in Macromolecular Chemistry, before moving to his present position as full professor at the University of Konstanz in 2004. His research is focussed on functional-group-tolerant polymerization catalysis, regarding polymerization and deactivation mechanisms, the generation of crystalline and luminescent nanoparticles, and conversion of renewable ressources.

Looking at the progress made in the development of new activators during the last 15 years, it appears that especially specialized companies like Albemarle continue to increase the catalyst efficiencies by improving aluminoxanes, especially for supported single-site catalysts. The development is mostly focused on combining good catalyst productivity together with obtaining the proper morphology of the polymer products. However, the examples of Collins, Busico, and Stephan show that also for solution processes optimizations are possible. Both metallocene and non-metallocene catalyst efficiencies can also be significantly increased by fine-tuning the activator/scavenger systems through in situ chemical modification. This may facilitate the industrial application of non-metallocene catalysts although most of these chemicals used will end up in the final polymer resin, which may negatively impact secondary polymer properties, such as the amount of volatile compounds, smell, blooming, and fogging.

3. Cyclopentadienyl–Amido Catalysts

In the production of linear low-density polyethylene (LLDPE), heterogeneous Ziegler catalysts have been strongly complemented by non-metallocene metal complexes. The so called constrained geometry catalysts (CGCs), which were commercialized by Dow with their homogeneous polymerization technology (termed INSITE), possess high activity, temperature stability, and comonomer incorporation.[31,32] These catalysts are based on a ligand design that Bercaw introduced for the preparation of organoscandium olefin polymerization catalysts, namely ansa-cyclopentadienyl–amido ligands.[33] Shortly after, Okuda published the synthesis of an ansa-cyclopentadienyl–amido titanium complex,[34] and researchers at Dow[35] and Exxon[36] developed Group 4 complexes of this type for olefin polymerization. These complexes usually consist of a η^5-coordinated cyclopentadienyl moiety that is covalently linked to a κ-coordinated amido group (Figure 2). Typically, a short $SiMe_2$ bridge is employed as a linker, which results in a strained geometry with a small Cp-M-N ligand bite angle of 107.6° at the metal for complex **1**. The strained geometry leads to a sterically open metal center, which is presumed to be the reason for their high comonomer incorporation ratios and activities.[37]

Typically, these complexes are synthesized by metathesis of the bislithiated ligand with $[MCl_4(thf)_2]$ (M = Ti, Zr, Hf),



1 **2** **3**

Figure 2. Structures of cyclopentadienyl–amido complexes.

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but for titanium this route often leads to low yields. This problem can be overcome by employing [$TiCl_3(thf)_3$] in the metathesis step and subsequent oxidation by AgCl, $PbCl_2$, or CH_2Cl_2.[38,39] Also other approaches have been studied, such as metalation with amido or benzyl transition-metal compounds or a templated synthesis route where the ligand is assembled on the metal center (Figure 3).[32,40]

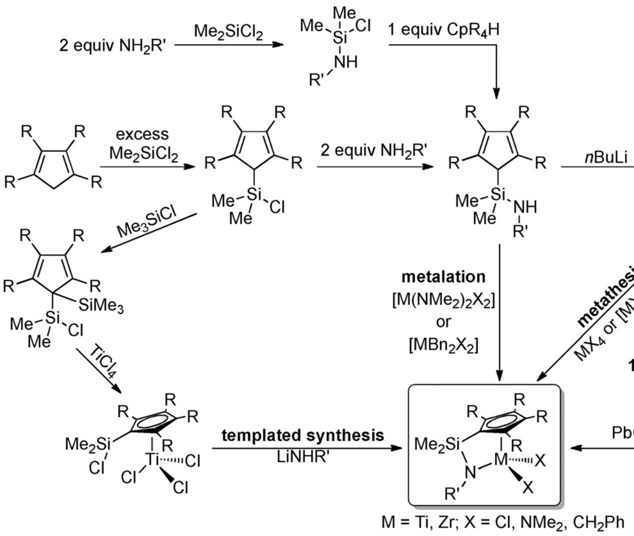

Figure 3. Synthesis of cyclopentadienyl–amido complexes.

Studies of structure–activity relationships by Dow showed that more electron deficient Cp ligands compared to tetramethylcyclopentadienyl resulted in lower activity and comonomer incorporation. For the substituent on the nitrogen atom, a similar trend was observed. The nature of the bridging unit has a strong influence on the catalyst properties. An elongation of the bridge to $(SiMe_2)_2$ in complex **2**, resulting in a larger Cp-Ti-N angle of 120.5°, leads to lower activity (6.6×10^6 g(polymer) mol(Ti)$^{-1}$ h^{-1}) and comonomer incorporation compared to complex **1** (4.3×10^7 g(polymer) mol(Ti)$^{-1}$ h^{-1}) with MAO activation. The ethylene-bridged complex **3**, which is quite similar to **1** in terms of the Cp-Ti-N angle (107.9° vs. 107.6°), exhibits a higher activity (1.6×10^8 g(polymer) mol(Ti)$^{-1}$ h^{-1}) but also lower comonomer incorporation than **1**.[37] As MAO is quite costly and large excesses (500–5000 eq) are required for smooth activation, boron-based activators, such as $B(C_6F_5)_3$ in combination with alkylated catalyst precursors, were also investigated. In this way, extremely high activities exceeding 10^9 g(polymer) mol(Ti)$^{-1}$ h^{-1} could be achieved.[41] In contrast to common metallocene catalysts, CGCs are able to produce high-molecular-weight polymers at temperatures up to 160 °C, even though molecular weights decrease with increasing temperature.[41]

Owing to their sterically open geometry, polymers obtained from cyclopentadienyl–amido catalysts are mostly atactic, especially when prepared at industrially relevant temperatures above 140 °C.[37]

Further enhancement of polymer molecular weights was achieved by the development of indenyl complex **4** bearing an additional nitrogen substituent on the five-membered hydrocarbon ring structure (Figure 4). This catalyst is capable of producing high-molecular-weight copolymers ($M_w = 2.8\times10^5$ g mol^{-1}, $M_w/M_n = 2.1$) with a high activity of 2.4×10^9 g(polymer) mol(Ti)$^{-1}$ h^{-1} at a polymerization temperature of 140 °C. Even at 160 °C, only slightly lower molecular weights are obtained.[42]

A sterically expanded constrained geometry catalyst **5** was synthesized by Miller and coworkers by replacing the cyclopentadienyl group on the ligand by an octamethyloctahydrodibenzofluorenyl moiety. This catalyst exhibits high 1-olefin homopolymerization activities, which are on the same order as for ethylene polymerization. This allows for the preparation of ethylene/4-methyl-1-pentene and ethylene/1-octene copolymers with virtually any composition at high activities. Even 4-methyl-1-pentene/1-octene copolymers can be obtained.[43] Propylene polymerization with complex **5** at −15 °C yields highly syndiotactic polypropylene ([rrrr] > 99 %) with a melting point of $T_m = 165$ °C. However, polypropylene molecular weights are only moderate ($M_n = 2.6\times10^4$ g mol^{-1}).[44]

Constrained-geometry catalysts are employed on a large scale in high-temperature solution processes for the production of copolymers of ethylene and higher 1-olefins, such as 1-hexene, 1-octene, and 1-decene, with up to 60 wt % of comonomer incorporated (marketed under Dow's ENGAGE and AFFINITY brands).[41] Catalysts for the production of HDPE and LLDPE in the Innovene gas-phase process were developed by BP (now INEOS) in collaboration with Dow. These catalysts are termed INcat HPLL (high-performance linear low) and are used for the production of INEOS' Eltex PF LLDPE resins and polyethylene of raised temperature resistance (PE-RT) for hot-water pipe applications (Eltex TUB 220-RT).[45] Further, a solution EPDM production process based on the INSITE catalyst technology was developed by DuPont Dow Elastomers (now Dow) whose polymers are marketed as Nordel IP,[46] as well as a gas-phase polymerization EPDM (termed Nordel MG) process employing constrained geometry catalysts in the Unipol process. To avoid sticking of the particles in the gas-phase EPDM process, carbon black is added to the polymerization reactor. This enables the production of granular EPDM resins with high

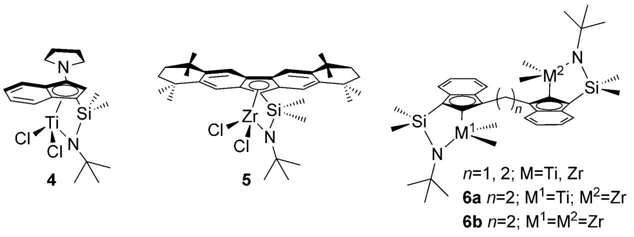

Figure 4. Structures of cyclopentadienyl–amido complexes.

Mooney viscosity.[47] However, the Nordel MG production plant in Seadrift, TX, was shut down in 2008 in the course of restructuring measures.[48]

The LLDPEs produced by CGCs possess narrow molecular weight and homogeneous comonomer distributions, which is suggested to afford superior mechanical properties compared to LLDPEs prepared by conventional heterogeneous Ziegler catalysts.[49] Usually, polymers with narrow molecular-weight distributions possess an unsatisfactory melt processability. A typical feature of these copolymers is their long-chain branches, occurring in homo- as well as copolymerization. Such long-chain branches are advantageous for processability, as illustrated most prominently by LDPE from free-radical high-pressure polymerization.[49,50] These long-chain branches are formed by insertion of vinyl terminated polymer chains as macromonomers into the growing polymer chain.[41] Experimental as well as computational studies suggest that almost exclusively vinyl terminated polymer chains are formed during polymerization,[51] with β-H transfer to the monomer being the energetically most favored termination pathway.[52,53] As an extension of this concept, tandem catalysis processes were developed for the CGC catalyzed copolymerization of ethylene with vinyl terminated oligoethylene macromonomers, which are produced in situ by a second oligomerization catalyst.[32] Even a heterobinuclear complex **6a** combining both active sites was developed. Owing to the spatial proximity of both metal centers, there is a high probability that vinyl-terminated oligomers formed by the Zr catalyst are enchained by the high-molecular-weight polymer-producing Ti center.[54]

Also other binuclear cyclopentadienyl–amido catalysts have been studied extensively for olefin polymerization by Marks and co-workers.[55,56] For the binuclear ethylene-bridged zirconium complex **6b**, higher molecular weights and comonomer incorporation rates compared to the mononuclear analogue were achieved. Most interesting, a significantly higher level of ethyl branches was observed, which was attributed to a reinsertion of a vinyl terminated polymer chain into the metal–ethyl bond after β-H transfer to the monomer. Agostic interactions of polymer bound protons to the second metal center are presumed to retain the vinyl terminated polymer chain in close proximity to the first metal center.[57] Bimetallic titanium catalysts were generally much more active than the zirconium complexes and efficiently copolymerized ethylene with sterically hindered 1-olefins such as isobutene, methylenecyclopentane and methylenecyclohexane. 2-Methyl-2-butene was incorporated by isomerization to 2-methyl-1-butene followed by rapid enchainment.[56]

Another class of material, which is accessible by constrained geometry catalysts, is ethylene–styrene copolymers. High polymerization activities and up to 50 mol% of styrene incorporation were achieved.[35,50,58] However, the styrene content is restricted to this value, as styrene homopolymerization and thus consecutive head-to-tail styrene insertion is highly unfavorable. In these ethylene–styrene copolymers, consecutive styrene enchainment is exclusively observed in a tail-to-tail fashion and ethylene insertion is highly favored over styrene insertion.[35,58] This limitation can be circumvented by application of 3,3′-diaryl-Cp substituted or binuclear titanium cyclopentadienyl–amido catalysts.[55,56,59] For the usual mononuclear complexes an intramolecular coordination of the phenyl ring to the metal center in the 2,1-insertion product is presumed to deactivate the catalyst. In the binuclear catalysts, either the arene moiety of the last inserted monomer can coordinate to the adjacent metal center, to allow coordination and insertion of further styrene monomers, or the second metal center assists during further styrene enchainment.[60] Ethylene/styrene copolymerization with aryl substituted CGCs is presumed to proceed by a similar mechanism. The aryl substituents are able to interact with the phenyl moiety of the styrene monomer and thus enhance styrene enchainment.[59] Dow produced these ethylene/styrene copolymers (termed INDEX ethylene/styrene interpolymers) in a large pilot plant, however, production was shut down in 2002 as no profitable business could be established.[61]

Catalysts structurally related to constrained geometry catalysts were developed by DSM for the preparation of ethylene propylene diene monomer (EPDM) rubbers. These catalyst precursors possess a Ti^{III} center and are termed as low-valency catalysts (Lovacat; Figure 5).[62,63] Nova Chemicals disclosed a phosphole catalyst (Figure 5), which is capable of producing high-molecular-weight LLDPEs at high temperatures with somewhat broad molecular-weight distributions, and may be applied in their Advanced Sclairtech solution polymerization process.[64]

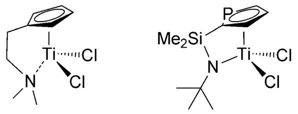

Figure 5. Chemical structures of DSM's Lovacat (left) and Nova Chemicals' phosphole catalyst (right).

A related catalyst system for LLDPE production, termed PHENICS (phenoxy-induced complex of Sumitomo), was developed by Sumitomo Chemical (Figure 6).[65,66] These catalysts typically possess a silicon-bridged cyclopentadienyl phenoxy ligand coordinating to a Ti^{IV} center. When complex **7** is activated with $i\mathrm{Bu}_3\mathrm{Al}/[\mathrm{Ph}_3\mathrm{C}][\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]$ high-molecular-weight ethylene/1-hexene copolymers are obtained with an activity of 2.7×10^7 g(polymer) mol(Ti)$^{-1}$ h^{-1} at a polymerization temperature of 80 °C. At a polymerization temperature of 180 °C and $i\mathrm{Bu}_3\mathrm{Al}/[\mathrm{PhNHMe}_2][\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4]$ activation, an activity of 6×10^6 g(polymer) mol(Ti)$^{-1}$ h^{-1} was achieved with complex **7**.

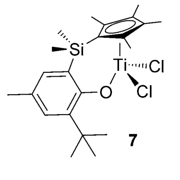

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Figure 6. Structure of PHENICS catalyst.

The substituents on the silicon bridge were found to have a significant impact on the regioselectivity of 1-olefin enchainment and owing to a high probability of chain termination after 2,1-insertion also on molecular weights. Increasing the steric bulk of these substituents hampers 2,1-insertion in propylene homopolymerization and leads to higher molecular weights.[67] Further catalyst optimization

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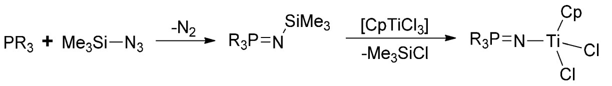
lead to complexes bearing thiophene-fused cyclopentadienyl moieties[68] or a fluorenyl ligand,[69] which were highly active in producing high-molecular-weight ethylene/1-hexene copolymers with high 1-hexene content even at temperatures up to 210 °C.

4. Phosphinimide Catalysts

Phosphinimide transition-metal olefin polymerization catalysts were developed by Stephan and co-workers based on the idea of mimicking a cyclopentadienyl ligand with synthetically readily accessible compounds. Earlier work by Wolczanski et al. describes a steric similarity between cyclopentadienyl and tri-*tert*-butylmethoxide,[70] which is sterically related to bulky phosphinimides (Figure 8). Furthermore, an electronic analogy between phosphinimide and cyclopentadienyl ligands has been proposed by Dehnicke and co-workers.[71] These facts lead to the assumption that Group 4 metal complexes bearing phosphinimide ligands should be efficient olefin polymerization catalysts upon activation with a suitable activator.[72,73] A variety of phosphinimide ligands and complexes thereof have been described.[74] They can be synthesized by Staudinger reaction[75] of readily available phosphines with azides such as Me_3SiN_3. From the trimethylsilylphosphinimines obtained, Stephan and co-workers synthesized the corresponding $[CpTi(NPR_3)Cl_2]$ complexes by Me_3SiCl elimination (Figure 7).[73]



$$PR_3 + Me_3Si{-}N_3 \xrightarrow{-N_2} R_3P{=}N(SiMe_3) \xrightarrow[-Me_3SiCl]{[CpTiCl_3]} R_3P{=}N{-}Ti(Cp)Cl_2$$

Figure 7. Synthesis of phosphinimines and the corresponding $[CpTi(NPR_3)Cl_2]$ complexes.

These complexes possess a pseudotetrahedral structure with an almost linear P-N-Ti geometry and Cp-Ti-N angles ranging from 120° to 125°. The phosphinimide ligands have a similar cone angle as cyclopentadienyl, but the steric bulk is somewhat retracted from the metal center. This leads to an efficient shielding of the metal center, but at the same time to a sterically more open geometry, which is beneficial for the reactivity of the resulting complexes (Figure 8).[76]

Ethylene polymerization with the MAO-activated catalysts at 25 °C resulted in low activities and bimodal molecular weight distributions for $[CpTi(NPCy_3)Cl_2]$ and $[CpTi(NP\mathit{i}Pr_3)Cl_2]$, whereas with $[CpTi(NP\mathit{t}Bu_3)Cl_2]$ an activity of 6.5×10^5 g(polymer) mol(Ti)$^{-1}$ h^{-1} and molecular weights of 9×10^4 g mol^{-1} with $M_w/M_n = 1.6$ could be achieved. By methylation of the dichloro catalyst precursors with MeMgBr to the corresponding $[CpTi(NPR_3)Me_2]$ complexes and subsequent activation with $[Ph_3C][B(C_6F_5)_4]$ significantly higher activities were obtained.[73,76] It is believed that MAO or residual $AlMe_3$ opens up considerable deactivation pathways for these complexes, leading to lower activities or bimodal molecular-weight distributions.[72,77] Model reactions of $[CpTi(NPR_3)Me_2]$ with $AlMe_3$ resulted in the formation of Ti-Al-carbide complexes by multiple C−H activation, which are inactive for olefin polymerization.[78]

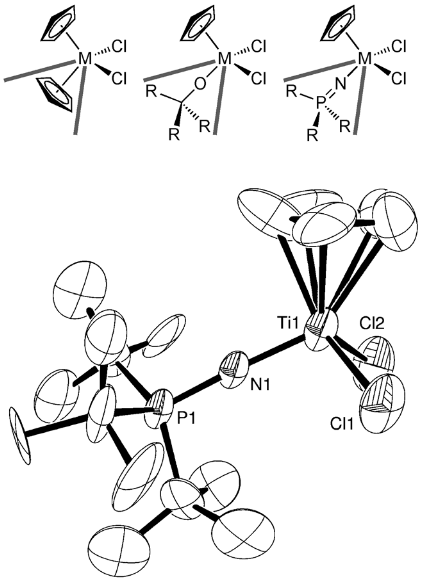
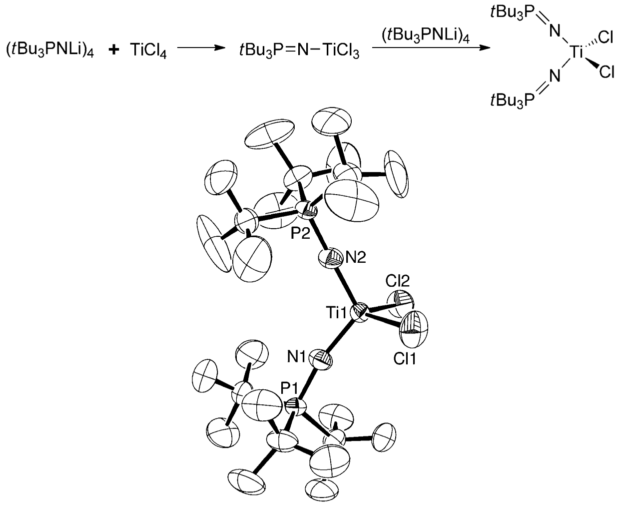


Figure 8. Cone angles of cyclopentadienyl, alkoxide, and phosphinimide ligands[72] and an ORTEP plot of $[CpTi(NP\mathit{t}Bu_3)Cl_2]$.[76]

Bulky substituents on the cyclopentadienyl ligand, for example *t*Bu or *n*Bu, generally increased the activity and polymer molecular weights of the corresponding complexes upon borate activation. However, the highest activity (2×10^6 g(polymer) mol(Ti)$^{-1}$ h^{-1}) was achieved with $[\mathit{n}BuCpTi(NP\mathit{t}Bu_3)Cl_2]$ by activation with MAO.[76]

Catalyst precursors of the type $[(\mathit{t}Bu_3PN)_nTiCl_{4-n}]$ were synthesized by reaction of $\mathit{t}Bu_3PNSiMe_3$ or $\mathit{t}Bu_3PNLi$ with $TiCl_4$ (Figure 9). Subsequent methylation could be performed with MeMgBr.[79,80] Ethylene polymerization studies of $[(\mathit{t}Bu_3PN)_2TiCl_2]$ showed low activities when activated with



$$(\mathit{t}Bu_3PNLi)_4 + TiCl_4 \longrightarrow \mathit{t}Bu_3P{=}N{-}TiCl_3 \xrightarrow{(\mathit{t}Bu_3PNLi)_4} (\mathit{t}Bu_3P{=}N)_2TiCl_2$$

Figure 9. Synthesis of $[(\mathit{t}Bu_3PN)_nTiCl_{4-n}]$ ($n = 1,2$) and an ORTEP plot of $[(\mathit{t}Bu_3PN)_2TiCl_2]$.[79]

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MAO. Model reactions with $AlMe_3$ again revealed decomposition products formed by C–H activation.[81] However, $[(tBu_3PN)_2TiMe_2]$ activated with borates yielded highly active ethylene polymerization catalysts. An activity of 1.2×10^6 g(polymer) mol(Ti)$^{-1}$ h^{-1} was achieved with $[(tBu_3PN)_2TiMe_2]$ by activation with $[Ph_3C][B(C_6F_5)_4]$ at 25 °C and 1 bar of ethylene. Under commercially relevant high-temperature continuous-flow solution polymerization conditions (160 °C, ca. 100 bar ethylene pressure), an activity of 6.2×10^7 g(polymer) mol(Ti)$^{-1}$ h^{-1} and a molecular weight of 7.8×10^4 g mol^{-1} could be achieved. The molecular weight distribution was $M_w/M_n = 1.9$, confirming the single site behavior of the catalyst even under these drastic reaction conditions. Under the same conditions, activities of 1.6×10^7 and 8.9×10^6 g(polymer) mol(metal)$^{-1}$ h^{-1} were obtained with the commercially widely employed constrained geometry catalyst $[(C_5Me_4SiMe_2NtBu)TiMe_2]$ and metallocene $[Cp_2ZrMe_2]$, respectively.[79]

The catalysts $[(R_3PN)_2TiX_2]$ and $[CpTi(NPR_3)X_2]$ are most likely employed in Nova Chemicals' high-temperature dual-reactor solution polymerization process (Advanced Sclairtech) for the production of ethylene/1-olefin copolymer resins with multimodal molecular weight or composition distributions (marketed as SURPASS). $[CpTi(NPR_3)X_2]$ is probably also used as a supported catalyst for gas phase polymerization.[82]

Related zirconium complexes with phosphinimide ligands were also investigated, but they were generally less active and more prone to deactivation reactions.[83]

Further developments lead to phosphinimide–phosphinimide,[84] chelating phosphinimide,[85] or bimetallic phosphinimide complexes,[86] but all of them showed low activities and were prone to deactivation. A more promising modification are the trisamido–phosphinimide complexes. Theoretical calculations suggest that more electron donating phosphinimide ligands would increase polymerization activity. Readily available triaminophosphines were employed for the synthesis of bulky, electron-rich tris-amido–phosphinimines and the corresponding titanium complexes (Figure 10). Ethylene polymerization activities with MAO activation were low and increased with increasing bulk at the phosphinimide ligand. By $B(C_6F_5)_3$ activation of $[Cp^*Ti(NP(NnPr_2)_3)Me_2]$, an activity of 2×10^7 g(polymer) mol(Ti)$^{-1}$ h^{-1} at 30 °C and 2 bar ethylene could be achieved.[87]

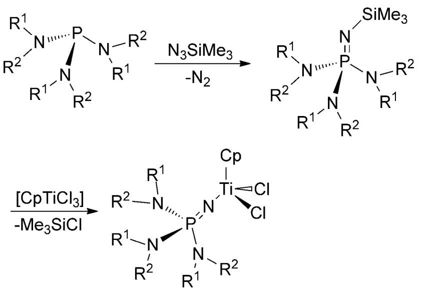

Figure 10. Synthesis of tris-amido–phosphinimide complexes.

5. Ketimide and Amidinate Complexes for EPDM Production

Group 4 transition-metal ketimide complexes with the general structure $[Cp'M(N{=}CR^1R^2)X_2]$ ($Cp' = C_5H_5$, C_5Me_5, indenyl, fluorenyl; M = Ti, Zr, Hf; X = Cl, Me, Bn) were disclosed by Nova Chemicals; these complexes are claimed to be highly active olefin homo- and copolymerization catalysts in gas phase, slurry, and high-temperature solution polymerization.[88] Highest activities in ethylene polymerization were achieved with bis(*tert*-butyl)ketimide ($N{=}CtBu_2$)-ligated titanium complexes (**8**; Figure 11).[89–92] Surprisingly, the activities increased dramatically in ethylene/1-hexene copolymerization to more than 10^9 g(polymer) mol(Ti)$^{-1}$ h^{-1} for $[(indenyl)Ti(N{=}CtBu_2)Cl_2]$ activated with a large excess of MAO.[91] $[Cp^*Ti(N{=}CtBu_2)Cl_2]$ **8** activated with MAO was even able to copolymerize ethylene and styrene in a living manner, although both homopolymerization reactions are not living.[93]

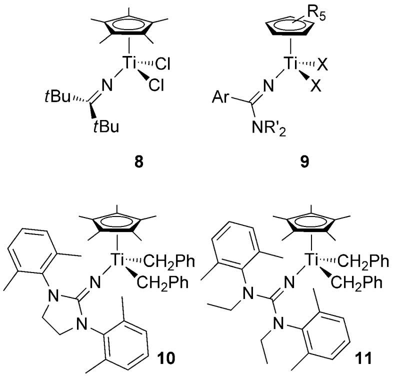

Figure 11. Structures of ketimide, amidinate, iminoimidazolidine, and guanidinate catalysts.

DSM Elastomers licensed this type of catalysts from Nova Chemicals for the production of a new ethylene propylene diene monomer (EPDM) rubber product, marketed under the trade name Keltan ACE ("advanced catalysis elastomers"). The catalyst structure was further improved, resulting in amidinate complexes **9** of the general structure $[(C_5R_5)Ti\{N{=}C(Ar)NR'_2\}X_2]$ (X = Me or Cl).[94–96] Kretschmer et al. reported an iminoimidazolidine catalyst **10**, which is highly active in ethylene and ethylene/1-olefin copolymerization especially in the presence of partially hydrolyzed iBu_3Al (TIBAO) as a scavenger, which seems to deactivate ketimide catalysts.[97] Guanidinate ligands (**11**) were employed by researchers at DSM to produce highly active catalysts.[98] All of these catalysts are highly active in ethylene propylene diene terpolymerization and are able to produce EPDM with relatively high contents of 5-vinylnorbornene incorporated as a diene monomer, which is almost exclusively enchained by its strained cyclic double bond. By comparison to conventional Ziegler–Natta catalysis, this suppresses formation of long-chain branches and cross-links, which lead to gelation during polymerization, reactor fouling, and unfavorable polymer properties. Vinylnorbornene containing EPDMs can be very

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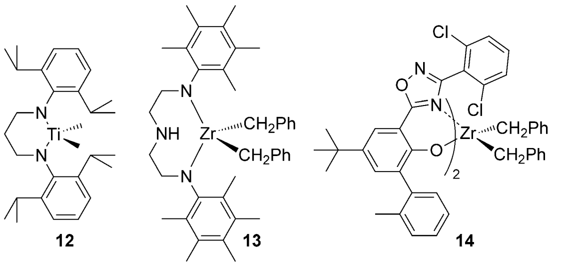
efficiently cross-linked by peroxide initiators. Low initiator and additive contents are required, which is beneficial for materials performance.[96,99] In 2011, Lanxess acquired DSM's elastomer business, including the Keltan ACE polymers.[100] Since mid-2013, Lanxess' largest EPDM plant at the Sittard–Geleen site, Netherlands, has been converted to ACE technology with a capacity of 95000 tons per year.[101] A new 160000 tons per year Keltan ACE plant in China, which will be supplied with ethylene and propylene from a methanol-to-olefin plant, is supposed to start production in 2015.[102] These Keltan ACE plants allow for a more economical and less-energy-consuming production of EPDM elastomers compared to classical vanadium catalysts, as the catalyst can withstand higher temperatures and thus less cooling is required. The highly active catalysts further avoid the de-ashing step of the final products.

6. Diamido Catalysts for Bimodal Polyethylene Production

Group 4 complexes bearing diamide ligands have been studied for olefin polymerization, owing to their higher electrophilicity compared to other complexes. McConville and co-workers synthesized titanium diamide complexes [(ArN(CH$_2$)$_3$NAr)TiR$_2$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$; R = Cl, Me, Bn) for the polymerization of 1-hexene with activities up to 3.5×10^8 g(polymer) mol(Ti)$^{-1}$ h^{-1} for complex **12** (Figure 12) activated with MAO.[103] Upon B(C$_6$F$_5$)$_3$ activation of the titanium methyl complex **12**, 1-hexene polymerization at room temperature proceeds in a living fashion, as the major chain termination pathway, namely chain transfer to aluminum, is avoided.[104] The zirconium analogues did not display significant olefin polymerization capabilities. However, owing to the high Lewis acidity of the coordinatively unsaturated cationic metal center, the polymerization activity of these catalysts is highly sensitive towards solvent and activator choice. Toluene readily coordinates to the activated catalysts and thus decreases the activity.[103]



12 **13** **14**

Figure 12. Structures of diamido, diamido–amine, and oxadiazol complexes.

To make these catalysts more stable, Schrock and co-workers developed diamide ligands possessing an additional amine donor in the ligand backbone. The complex [((MesNCH$_2$CH$_2$)$_2$NR)ZrMe$_2$] (Mes = mesityl; R = Me, H) activated with [Ph$_3$C][B(C$_6$F$_5$)$_4$] was used for 1-hexene polymerization.[105] The cationic polymerization active complexes undergo CH activation of the *ortho* methyl group of the mesityl substituents as a major deactivation pathway.[106] Slurry ethylene/1-hexene copolymerization with [((MesNCH$_2$CH$_2$)$_2$NH)ZrMe$_2$] supported on silica/MAO yields copolymer with an activity of 3×10^7 g(polymer) mol(Zr)$^{-1}$ h^{-1}.[107] Patents by Univation Technologies LLC indicate that, diamido complexes of the type [((Me$_5$C$_6$NCH$_2$CH$_2$)$_2$NH)ZrBn$_2$] **13** are used in combination with metallocenes such as [*n*PrCp(Me$_4$C$_5$H)ZrCl$_2$] for the production of bimodal HDPE resins (marketed as PRODIGY) in their Unipol process.[108,109] In this process, the two catalyst precursors are immobilized together on one support material, such as silica, to produce a bimodal PE reactor blend in a single fluidized-bed gas-phase reactor.[110] The metallocene catalyst, which has a high H$_2$ response, produces the low molecular weight (ca. 5–35 × 10^3 g mol^{-1}) part and the diamido complex the high-molecular-weight fraction (ca. 4–7 × 10^5 g mol^{-1}). These bimodal PE resins are for example well-suited for long-lasting pressure pipe (PE 100 standard) applications. For a better controllability of the multimodal PE composition an oxadiazol containing complex **14**, exhibiting essentially no hydrogen response, was described. In this way the molecular weight of one component of the polymer blend stays constant, independent of the hydrogen partial pressure, whereas the molecular weights of the other components can be adjusted.[111]

7. Imino–Amido Catalysts

Imino–amido Group 4 complexes were developed by researchers at Union Carbide.[112] Complexes of type **15** can be prepared by reaction of α-diimine ligands with MBn$_4$ (M = Hf, Zr) by transfer of one benzyl group to the ligand backbone. However, complexes synthesized by this procedure exhibit multisite behavior in olefin polymerization, because these imino–amido complexes can undergo various side reactions, especially at elevated temperatures.[113] When prepared from α-di(aldimine) ligands, a second benzyl group can be transferred to the ligand backbone under formation of the corresponding diamido complex **18b**.[114] For other complexes, double-bond isomerization from the imine to the amide (**16**) or dibenzyl elimination from the imino–amido complexes to an ene-diamido complex **17a** was observed (Figure 13).[113]

More defined polymerization catalysts could be obtained by employing trimethylethylidene-bridged imino–amino ligands in the synthesis of the imino–amido Group 4 complexes (Figure 14). Complex **19** can be synthesized by reaction of the imino–amino ligand with MBn$_4$. Methyl complexes can be prepared by reaction of the deprotonated ligand with MCl$_4$ (M = Zr, Hf) and subsequent methylation with MeMgBr. At elevated temperatures, the alkylimine complex **19** and also the catalytically active cationic species undergo isomerization to the arylimine complex **20** by a 1,2-methyl shift reaction, which was evidenced by deuteration experiments and DFT calculations. The arylimine complex **20** is thermodynamically

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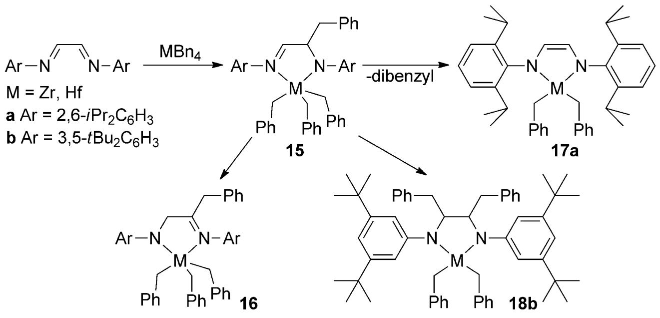

Figure 13. Synthesis and side reaction of imino–amido Group 4 complexes.

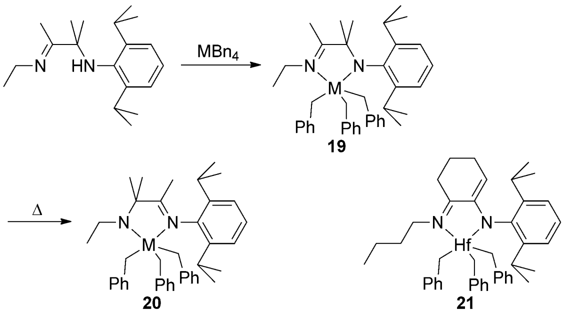

Figure 14. Synthesis and isomerization of imino–amido complexes (M = Zr, Hf) and structure of imino–enamido complex **21**.

favored, which is most likely due to steric repulsion of the backbone methyl groups and the isopropyl substituents in complex **19**. However, under industrially relevant polymerization conditions, the rate of this isomerization reaction is in the range of the catalyst lifetime, and thus does not affect the polymer properties. The hafnium and zirconium complexes of type **19** are highly active catalysts for ethylene/1-octene copolymerization at 120 °C when activated with a combination of MMAO and $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$. A high molecular weight polymer ($M_w = 6.3\times10^5\,g\,mol^{-1}$, $M_w/M_n = 3.1$) is obtained with the hafnium complex **19** at an activity of 5.6×10^8 g(polymer) mol(Hf)$^{-1}$ h^{-1}. For the zirconium analogue the activity is somewhat lower (3.7×10^8 g(polymer)-mol(Zr)$^{-1}$ h^{-1}), but the molecular weight is higher ($M_w = 7.8\times10^5\,g\,mol^{-1}$, $M_w/M_n = 2.8$). The polymerization activity of **20** was about 20 times lower in both cases and the catalysts exhibited multisite behavior resulting in multimodal molecular-weight distributions.[115]

To overcome these thermal instabilities, imino–enamido hafnium and zirconium complexes were investigated by researchers at Dow. Complex **21** (Figure 14) yields ultra-high-molecular-weight ethylene/octene copolymer ($M_w = 10^6\,g\,mol^{-1}$, $M_w/M_n = 2.4$) at an activity of 7.2×10^8 g(polymer) mol(Hf)$^{-1}$ h^{-1} when activated with $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$/MMAO at a polymerization temperature of 120 °C and does not undergo isomerization at elevated temperatures.[116] Imino–amido as well as imino–enamido hafnium and zirconium complexes can be used in Dow's chain-shuttling polymerization process for the preparation of polyolefin multiblockcopolymers (see below).

8. Pyridyl–Amido Catalysts

Pyridyl–amido complexes of the general structure **22** (Figure 15) were found to be highly active olefin polymerization catalysts with unique properties. These catalysts were studied by Dow in collaboration with the high-throughput screening company Symyx (now Freeslate).[117,118] The complexation of $Hf(NMe_2)_4$ with the *ortho*-phenyl-substituted ligand results in the formation of a cyclometalated product possessing a Hf–C(aryl) σ bond (Figure 15). In the case of the naphthyl-substituted derivative, this does not readily occur during the complexation step, but during subsequent methylation with $AlMe_3$ under the evolution of methane.[117]

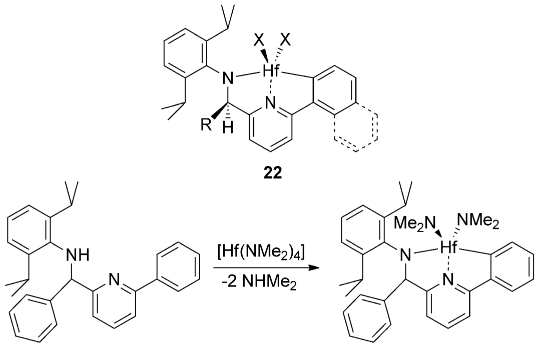

Figure 15. General structure **22** (R = H, aryl; X = Cl, Me, NR'$_2$) and synthesis of pyridyl–amido complexes.

Upon borate activation, the C_1-symmetric, methylated catalyst precursors are capable of polymerizing propene at high temperatures (> 90 °C) to an isotactic high-molecular-weight material.[117] Surprisingly, an isotactic enriched polypropylene is also obtained when C_s symmetric catalyst precursors, having no stereocenter, are employed.[119] This can be ascribed to the specific activation chemistry of these catalysts. Experimental as well as theoretical studies on the initiation reactions of this catalyst system revealed the insertion of an olefin into the Hf–C(aryl) bond to be favored over the insertion into the Hf–alkyl bond.[120–122] Liberation of 1 equiv of 1-butene from a pyridyl–amido hafnium dibutyl complex by $[Ph_3C][B(C_6F_5)_4]$ activation resulted in the formation of low-molecular-weight polybutene, with only a few percent of the metal centers being active. This indicates that the initial cationic species is inactive for polymerization and formation of a polymerization active catalyst by 1-butene insertion into the Hf–C(aryl) bond is much slower than chain propagation (Figure 16). Further evidence to such an activation pathway was provided by trapping and NMR spectroscopic verification of the Hf–C(aryl) insertion products by employing coordinating olefins such as 2-vinylpyridine.[121]

In the case of 1-olefin polymerization, this unusual activation reaction leads to the formation of various isomeric active cationic catalysts.[120,121] These can induce stereocontrol

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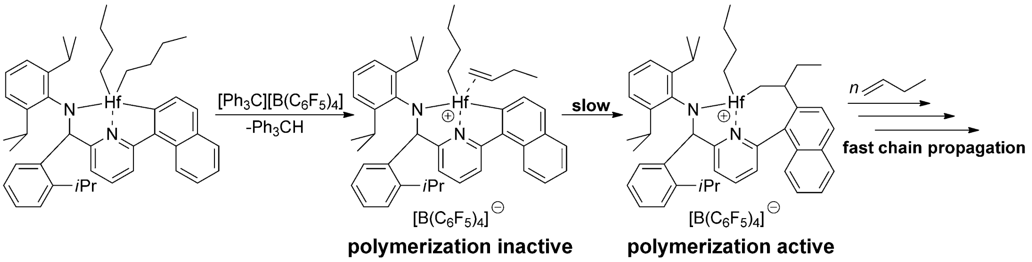


Figure 16. Mechanism of initiation of pyridyl–amido hafnium complexes.

to the polymerization reaction[119] or behave completely different in terms of activity or polymer molecular weights, thus leading to a multi-site catalyst.[123] In copolymerization reactions of, for example, ethylene and 1-olefins, this effect can be even more pronounced, as chemically different active sites are formed. In the case of ethylene/1-octene copolymerization, a broad molecular-weight distribution is observed by GPC, which can be fitted to a bimodal distribution. Increasing the 1-octene concentration shifts the distribution to the high-molecular-weight fraction, thus indicating that the high-molecular-weight polymer fraction is produced by the octene-inserted active species. Further, there is evidence that the octene-inserted species is also the more active one.[120]

Such pyridyl–amido hafnium catalysts are employed for the production of propylene-ethylene copolymers (Dow's VERSIFY) by solution polymerization technology. The polymers obtained are suggested to possess an advantageous broad melting range, good processability, and good optical clarity as a result of relatively narrow molecular-weight distributions, but broad composition distributions. Applications are fibers, blown films, soft-touch grips, sealants, hot melt adhesives, or in food packaging.[49,124]

Furthermore, pyridyl–amido hafnium polymerization catalysts are also used in the chain shuttling polymerization processes for the production of olefin block copolymers (see Section 10).

9. Phenoxyimine Catalysts

In 1995, Floriani and co-workers reported a salicylaldiminato-type zirconium complex, but with very low activity in ethylene polymerization.[125] Fujita and co-workers at Mitsui Chemicals further investigated phenoxyimine Group 4 transition-metal complexes for olefin polymerization (also termed FI catalysts from the Japanese pronunciation "Fenokishi-Imin").[126–128] The variation of the various substituents on the ligand framework yielded a versatile class of olefin polymerization catalysts with the general structure shown in Figure 17. The complexes are usually synthesized by reaction of the deprotonated Schiff base ligands, which are prepared by condensation of a salicylaldehyde with an amine, with MCl_4 (M = Ti, Zr, Hf). Most of these complexes exhibit a C_2-symmetric *cis*-X/*cis*-N/*trans*-O geometry.[126,128,129]

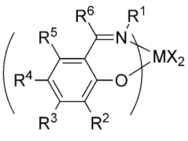
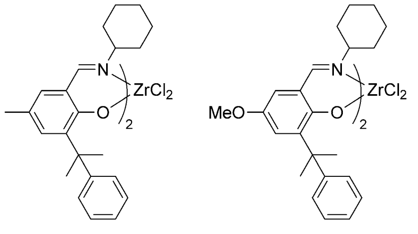


Figure 17. General structure of phenoxyimine complexes.

The substituents on the phenoxy group as well as the imine moiety (R^1 to R^6) have a strong impact on catalyst activities as well as polymer molecular weights in ethylene polymerization. For some of these substituents a clear structure–property relationship could be observed. For R^2, in general steric bulk is beneficial for activity and molecular weights. Higher steric bulk at R^1 leads to higher molecular weights but lower activity. Electron-donating substituents (for example, OMe) at R^4 improve the temperature stability of the catalyst.[126,129,130]

Group 4 salicylaldiminato complexes possess very high ethylene polymerization activities upon activation with MAO. With an activity of 4.3×10^9 g(polymer) mol(Zr)$^{-1}$ h^{-1}, complex **23** (Figure 18) is one of the most active ethylene polymerization catalysts at room temperature. This extraordinary high activity was further improved by the more temperature-stable complex **24** at the industrially more relevant temperature of 75 °C (7.2×10^9 g(polymer) mol(Zr)$^{-1}$ h^{-1}).[129]



23 **24**

Figure 18. Phenoxyimine complexes **23** and **24**.

A living polymerization catalyst was developed by Fujita and Coates independently by introduction of fluorine substituents to the aniline component of the ligand (Figure 19).[131,132] Various substitution patterns were investigated, but only *ortho*-fluorinated complexes perform living olefin polymerization. Fluorination on other positions only leads to higher activities owing to their electron-withdrawing nature.

The reason for this living behavior is not fully understood and is subject to controversial discussions.[133] Based on DFT calculations, Fujita and co-workers proposed a hydrogen bond between the fluorine substituents and the β-hydrogen atoms of the polymer chain, preventing β-hydrogen transfer to the titanium.[131b] A weak repulsive interaction between the *o*-F atoms and the growing polymer chain was suggested by Talarico and co-workers to suppress termination reactions in

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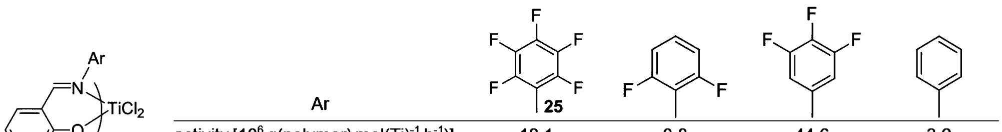

Ar	25			
activity [10^6 g(polymer) mol(Ti)$^{-1}$ h^{-1})]	18.1	0.8	44.6	3.2
M_n [10^3 g mol^{-1}]	424	64	98	1281
M_w/M_n	1.13	1.05	1.99	2.55

Polymerization conditions: 1 bar ethylene, 25 °C, 1–5 min (Ar = Ph: 50 °C, 30 min).

Figure 19. Ethylene polymerization with fluorinated phenoxyimine catalysts.[126]

the living polymerization of propylene with an *ortho*-fluorinated phenoxyimine catalyst.[134]

Yu and Mecking reported an *ortho*-fluorinated enolatoimine titanium complex, which is less reactive than the phenoxyimine complex, allowing an even more controlled living polymerization of ethylene at temperatures up to 75 °C.[135] This catalyst provides access to polyethylenes with an extremely narrow molecular weight distribution, for example, $M_w/M_n = 1.01$ at $M_n = 3 \times 10^5$ g mol^{-1}. Bryliakov et al. investigated the MAO generated cation of this system by NMR spectroscopy and found evidence for a noncovalent interaction of the *o*-F moieties with the metal center, which is presumed to suppress termination reactions.[136]

Not only ethylene but also propylene is polymerized by these *ortho*-fluorine-substituted phenoxyimine catalysts in a living fashion.[132] This living behavior, which is found for various monomers, provides access to a wide variety of well-defined olefin block copolymers.[126,137]

Surprisingly, most Group 4 phenoxyimine complexes polymerize propylene in a syndiospecific mode by 2,1-insertion, even though they are C_2-symmetric. This selectivity is even more pronounced for the fluorinated catalysts.[132b] A Δ/Λ site isomerization after each insertion step was proposed by Cavallo and co-workers to lead to this chain-end controlled stereoselectivity.[138,139] Activation with iBu$_3$Al/[Ph$_3$C][B(C$_6$F$_5$)$_4$] can turn the stereoselectivity to a highly isotactic fashion, which is believed to result from the reduction of the imine moieties to the corresponding aluminum-coordinated amines.[129,140,141] Further, phenoxyimine complexes bearing bulky R^6 substituents are able of polymerizing propylene isospecifically.[142]

Kol and co-workers investigated the structurally related Group 4 salan complexes (Figure 20) for the polymerization of 1-olefins, such as propylene and 1-hexene. Owing to their fixed geometry, these C_2-symmetric *cis*-X/*cis*-N/*trans*-O complexes produce highly isotactic polymers if steric bulk is present in the *ortho* position of the phenolic oxygen atom. The *tert*-butyl-substituted zirconium complex **26** yields poly(1-hexene) with an isotacticity of more than 95 %, but at a relatively low activity (1.8 × 10^4 g(polymer) mol(Zr)$^{-1}$ h^{-1}).[143] By replacing the bulky alkyl groups with iodine substituents and using a smaller metal center in complex **27**, isotactic high-molecular-weight poly(1-hexene) and polypropylene could be obtained at high activities.[144] Salalen titanium complexes possessing a rigid aminomethylpyrrolidine backbone (**28**) were even able to polymerize propylene to isotactic polypropylene with an isotacticity of [mmmm] of more than 99.6 % and a melting point of 170 °C. This is suggested to be the highest melting point for nascent polypropylene ever observed.[145]

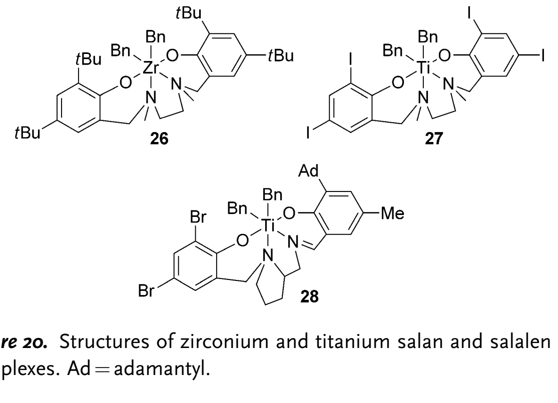

Figure 20. Structures of zirconium and titanium salan and salalen complexes. Ad = adamantyl.

Usually, bis-ligated MAO activated phenoxyimine catalysts possess low comonomer incorporation ratios in the case of higher 1-olefins. However, iBu$_3$Al/[Ph$_3$C][B(C$_6$F$_5$)$_4$] activation can lead to higher comonomer incorporation.[129,146,147] Furthermore, monoligated phenoxyimine complexes possessing an additional donor have higher reactivities towards 1-olefins, because they are less sterically crowded.[148,149]

For industrial slurry or gas-phase polymerization processes, a heterogenization of single-site catalysts is desirable. This is generally a challenge, as often catalyst activities (per metal center) and also selectivities are compromised. Usually MgCl$_2$ or SiO$_2$ are used as supports in combination with an activator, such as MAO or alkylaluminum compounds in combination with borates.[150] Fujita and co-workers employed MgCl$_2$/R$'_n$Al(OR)$_{3-n}$ as a support for phenoxyimine catalysts, which was prepared by reaction of the MgCl$_2$/ROH adduct with AlR$'_3$ (R = 2-ethylhexyl; R$'$ = iBu, Et). This support also functions as an activator, and activities comparable to the MAO activated catalysts were achieved. For supported Ti phenoxyimine complexes, narrow molecular-weight distributions were obtained in ethylene polymerization and even the living character of the fluorinated catalysts was retained in propylene polymerization. Supported zirconium phenoxyimine catalysts yielded spherical ultrahigh-molecular-weight polyethylene particles with high bulk densities (0.50 g mL^{-1}).[151]

Group 4 phenoxyimine complexes might be used for example for the preparation of end-functionalized polyethylene[152] or ultrafine ultrahigh-molecular-weight polyethylene particles.[153] A news article indicates that phenoxyimine complexes have been employed for gas-phase HDPE production on a pilot plant scale.[154] Further, phenoxyimine catalysts are applied in the chain shuttling polymerization process for the production of olefin block copolymer (see Section 10).

Rastogi and co-workers employed the living polymerization catalyst **25** for the preparation of disentangled ultra-

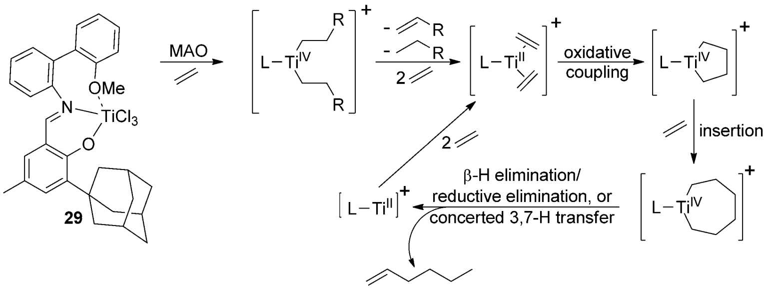

Figure 21. Proposed mechanism for ethylene trimerization using phenoxyimine catalysts.

high-molecular-weight polyethylenes (UHMWPEs).[157] UHMWPE has excellent mechanical properties, which are related to its high entanglement density, but this also complicates processing owing to the high melt viscosity. In the final shaped part, a high degree of entanglements is advantageous for mechanical properties, but for processing a low degree of entanglement is beneficial. To achieve this, the polymerization was carried out at low temperatures under high-dilution conditions, so that crystallization is faster than chain growth and entanglement between growing chains is suppressed. If the nascent disentangled polymer powder is melt-processed, entanglements are formed, which again complicate processing, but if the polymer is preheated to a temperature some degrees below the melting point, entanglement formation starts in the amorphous regions. This leads to a polymer consisting of disentangled domains in an entangled matrix, which still possesses a low plateau modulus and a significantly enlarged modulus build-up time. In this way, melt processing of UHMWPE is facilitated and final entanglement density in the injection-molded part can be increased by heating to high temperature for a certain time.[155,156] Further, disentangled UHMWPE can be used for the preparation of films, which can be stretched biaxially without the use of solvents to obtain a highly ordered crystalline UHMWPE film with high modulus and strength.[157]

Besides the aforementioned studies of olefin polymerization, phenoxyimine-type catalysts are also employed in the selective trimerization of ethylene to 1-hexene. Fujita and coworkers developed monoligated complexes bearing a pendant donor, which oligomerize ethylene with high activities to 1-hexene. The MAO activated complex **29** produces 1-hexene with a selectivity of 92% and an activity of 3.2×10^{8} g(1-hexene) mol(Ti)$^{-1}$ h^{-1} at 50 bar ethylene pressure and 30 °C, which is two orders of magnitude higher than for common chromium catalysts under similar conditions. The selectivity is explained by a mechanism involving a Ti^{II} center to which two ethylene molecules are oxidatively added by formation of a metallacyclopentane species. This inserts one further ethylene molecule followed by a β-H elimination/reductive elimination step to form 1-hexene and Ti^{II}. The involved Ti^{II} species is presumed to be generated from the bismethlyated cationic catalyst precursor by insertion of ethylene into both metal alkyl bonds and consecutive β-H elimination/reductive elimination (Figure 21).[158] Bercaw and co-workers conducted further mechanistic studies on a more defined catalyst system by methylation of **29** with MeMgBr and activation with $B(C_6F_5)_3$. These studies indicate that initiation is much slower than oligomerization and that the involved Ti^{II} species is generated by olefin insertion into one of the Ti−Me bonds followed by β-H elimination and reductive elimination of methane, which was confirmed by deuteration experiments.[159] Very recently, further mechanistic investigations on the reaction intermediates by NMR and EPR spectroscopy were reported by Talsi and co-workers.[160] Press releases by Mitsui Chemicals indicate that this catalyst technology is used in a 30000 tons per year 1-hexene plant, which started production in 2011.[161]

10. Chain-Shuttling Polymerization

Block copolymers are an interesting class of materials, which find application for example as thermoplastic elastomers. In these materials the elasticity of amorphous, low glass transition temperature (T_g) polymers can be combined with the strength of crystalline polymers. Commonly, block copolymers are prepared by living polymerization. The major drawback of this method is that only one polymer chain per initiator or active metal center is produced, which makes this process commercially unviable for expensive transition metal catalysts. This issue is overcome by a chain-shuttling polymerization process developed by Arriola and co-workers at Dow for the synthesis of olefin block copolymers (OBCs). In this solution polymerization process the growing polymer chain is transferred reversibly with a chain-transfer agent such as $ZnEt_2$ between a catalyst that does not incorporate comonomer significantly (for example, a phenoxyimine Zr complex), and a catalyst with a high propensity for comonomer incorporation (a pyridyl–amido Hf complex; Figure 22). This yields multiblock copolymers with highly crystalline polyethylene and amorphous poly(ethylene-co-1-olefin) blocks. As this polymerization system is not stoichiometric but catalytic in terms of polymer chains produced per metal center, commercially profitable polymer quantities can be produced with relatively low catalyst loadings.[162,163] Dow and Mitsui Chemicals entered a joint research agreement for the development of catalyst systems for the chain shuttling polymerization process in 2006.[164] The multiblock copolymers, which are marketed as INFUSE OBC by Dow, can be used for flexible parts fabricated by injection molding such as soft touch grips. Another application is for example the fabrication of flexible films for diapers. Very recently, Dow announced a new block copolymer product (termed INTUNE) on the basis of ethylene and propylene. These polymers are presumed to allow an efficient compounding of polypropylene with various nonpolar and polar polymers such as polyethylene, polyolefin elastomers, ethylene/vinyl alcohol copolymers, and polyamides.[165]

By using multifunctional chain-transfer agents, the chain shuttling concept was further expanded to the synthesis of

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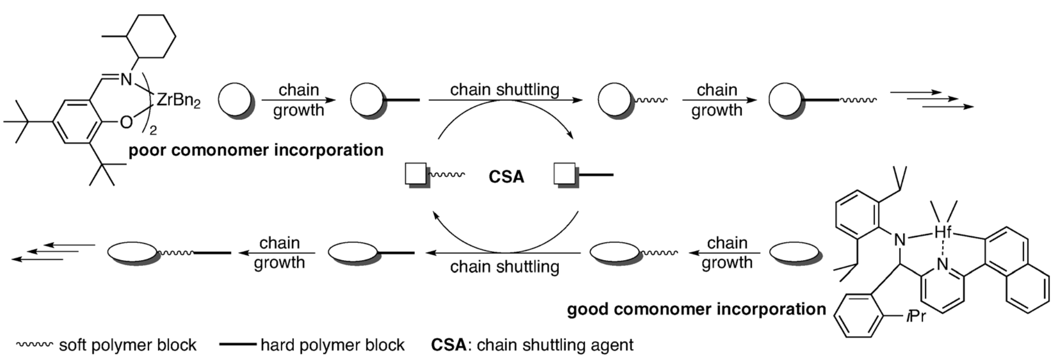
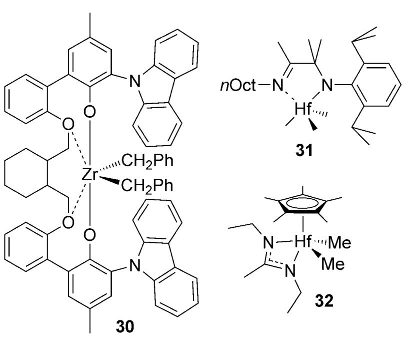


Figure 22. Chain-shuttling polymerization process, affording multiblock copolymers.[162a]

telechelic polymers and blockcopolymers, which can be employed as ingredients for coatings, sealants, adhesives, and rocket-fuel binder.[166,152] In this context, a double chain shuttling process is also mentioned, for which the cheaper and less pyrophoric aluminum alkyls can be employed as surrogates. As chain transfer to aluminum is not as efficient as to zinc, small amounts of zinc alkyl compounds are used to catalyze the chain transfer from the transition metal to the aluminum compound.[166a]

Besides phenoxyimine zirconium and pyridyl–amido hafnium complexes, additional post-metallocenes are referred to in the context of the chain shuttling polymerization process. These complexes include a broad variety of constrained geometry catalysts such as complex **4**, diamido–amine-coordinated hafnium complexes similar to complex **13** (see Section 6), the oxygen chelated complex **30**, and imino–amido complexes (see Section 7), such as **31** (Figure 23).[163,166] Imino–amido catalysts can be employed in the chain-shuttling process instead of the phenoxyimine catalyst to produce the hard block of the multiblock copolymer. The octene incorporation of these catalysts is slightly higher than of the phenoxyimine complex and can be adjusted by variation of substituents and the metal center, thus allowing for a fine tuning of the properties of the hard block.[167]

Another approach toward large scale production of precisely defined polyolefins with very narrow molecular weight distributions is the catalyzed chain growth (CCG) or catalytic chain transfer polymerization (CCTP).[168] In this process the polymer chain is transferred reversibly from the catalytically active metal center to a surrogate, typically a zinc or main-group-metal alkyl compound, with the chain transfer rate being faster than the chain growth rate. This leads to a simultaneous growth of all polymer chains and thus narrow molecular-weight distributions. The number of polymer chains is not stoichiometric in the costly catalyst, but in the much cheaper chain transfer agent. The metal-containing end groups of these polymers can be further converted into a great variety of functional groups. Various metals, including late and early transition metals and lanthanides, were employed as catalysts. Group 4 cyclopentadienyl acetamidinate complexes (**32**) in combination with chain-transfer agents were utilized by Sita and co-workers for the synthesis of various well-defined, end-functionalized polyolefins.[169] With this catalyst system, ethylene/1-hexene multiblock copolymers can be prepared by dynamic counterion exchange of a tightly ($[MeB(C_6F_5)_3]^-$) and a weakly binding borate anion ($[B(C_6F_5)_4]^-$), which leads to a modulation of the 1-olefin enchainment rate.[170] To decrease the amount of zinc alkyl compounds, a ternary chain-transfer system with aluminum alkyls as major component can be employed.[171]



30 **31** **32**

Figure 23. Structures of oxygen chelated complex **30**, imino–amido complex **31**, and acetamidinate complex **32**.

11. Cationic Late-Transition-Metal Ethylene Polymerization Catalysts

In 1995, Brookhart and co-workers reported that cationic $[Ni^{II}(diimine)]$ and $[Pd^{II}(diimine)]$ complexes polymerize ethylene to a high-molecular-weight, highly branched material (Figure 24).[172] This is due to a chain-walking[173] of the catalysts along the growing chain by a series of β-hydride elimination and reinsertion events, without loss of the growing chain from the metal site. Chain transfer is suppressed by bulky substituents of the diimine ligand, which block the axial coordination sites for incoming monomer (Figure 25). The active catalyst can be generated from the dihalide complexes such as $[(diimine)NiBr_2]$ with MAO. For Pd^{II}-catalyzed polymerization, typically isolated methyl complexes $[(diimine)PdMe(L)]^+Y^-$ or stable six-membered che-

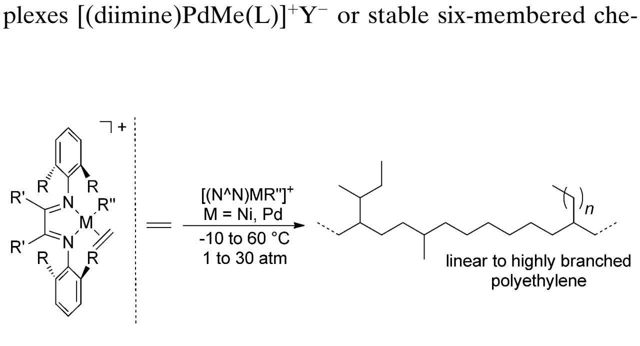


Figure 24. Ethylene polymerization by cationic Ni^{II} and Pd^{II} diimine catalysts.

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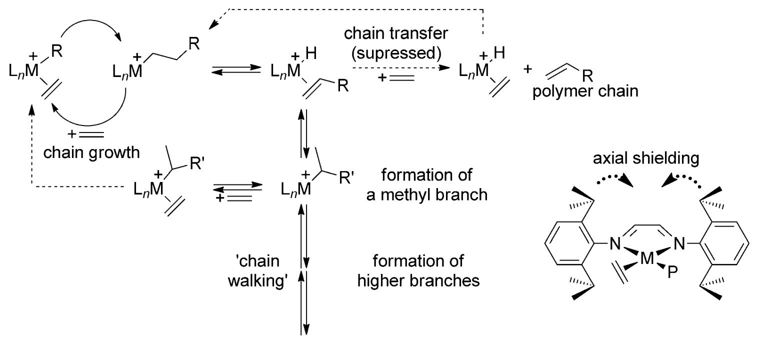

Figure 25. Mechanism of branch formation with cationic Ni^{II} and Pd^{II} diimine catalysts.[172]

lates resulting from insertion of acrylate into (in situ-generated) Pd–Me species are employed. Catalyst activities amount to several 10^8 g(polymer) mol(Ni)$^{-1}$ h^{-1} and 10^5 g(polymer) mol(Pd)$^{-1}$ h^{-1}, respectively.

The Pd^{II} catalysts provide high-molecular-weight ($M_n > 10^5$ g mol^{-1}), highly branched amorphous materials with about 100 branches per 1000 carbon atoms. The branching pattern contains methyl, ethyl, propyl, and higher branches and even branches on branches, that is a hyperbranched structure.[172,174] Remarkably, these catalysts allowed for the first insertion copolymerization of polar vinyl monomers, most prominently acrylates, with ethylene or 1-olefins.[175] Polymerization rates decrease with increasing acrylate incorporation, owing to chelating coordination of acrylate-based repeat units to the metal center, which reversibly blocks binding sites for further chain growth.

With Ni^{II} catalysts, the degree of branching depends on the diimine substitution pattern, polymerization temperature, and ethylene concentration.[176] By comparison to the Pd^{II}-based polymerizations, the polyethylenes formed with Ni^{II} diimines are rather dominated by methyl branches, in this sense there is an analogy to ethylene–propylene copolymers. Note that the cationic [Ni(diimine)] catalysts have been reported to copolymerize ethylene with acrylate to a linear polymer in a slow reaction.[177]

Terphenyl-substituted diimines (R = phenyl or substituted phenyl in Figure 24) provide more temperature stable Ni^{II} catalysts, which have a significant lifetime at typical polymerization process temperatures of 80 °C. At the same time, the degree of branching is reduced toward a linear microstructure, however.[176,178,179] Molecular weights can be influenced by the addition of hydrogen for these catalysts. As for related neutral salicylaldiminato Ni^{II} complexes,[180] remote substituents, particularly in the 3′,5′-position of the N-terphenyl motif, can enhance branching of ethylene homopolymers.[181] The synthetically elegant cyclophane motif also provides relatively temperature-stable Ni^{II} catalysts that polymerize ethylene to high-molecular-weight, highly branched polymers with relatively narrow molecular-weight distributions that are as low as $M_w/M_n = 1.23$ (at 50 °C polymerization temperature).[182] Supported versions of the [Ni(diimine)] catalysts have been reported, employing silica mostly, and studied in slurry as well as gas-phase polymerization.[183–189]

Initiated by the aforementioned findings, structurally related iron catalysts (Figure 26) were reported by Brookhart and co-workers, Gibson et al., and A. Bennett of DuPont.[190–194] A cross-licensing agreement was later announced between DuPont and BP Chemicals.[195] The iron catalysts polymerize ethylene with high rates (up to 3.3×10^8 g(polymer) mol(Fe)$^{-1}$ h^{-1}) to a strictly linear polymer of typically $M_n \approx 5 \times 10^4$ g mol^{-1}. Molecular-weight distributions are typically rather broad owing to chain transfer to the aluminum cocatalyst. Iron pyridyl–diimine complexes with less bulky N-aryl substituents (R = H in Figure 26) oligomerize ethylene very selectively to linear 1-olefins with high rates exceeding those reported for the neutral κ^2-*P,O*-coordinated Ni^{II} catalysts used on a large scale in the Shell higher olefin process (SHOP).[196] A high selectivity for ethylene over 1-olefins is also a specific feature of the iron-based ethylene polymerization catalysts; 1-olefins are typically not incorporated. Reactor blends with hybrid catalysts containing these late-transition-metal centers in combination with early-transition-metal insertion polymerization catalysts (metallocenes, post-metallocenes or classical Ziegler catalysts) have been developed.[183,197–199] Polymerization in the presence of ethylene and a 1-olefin such as butene or 1-hexene yields a linear medium-molecular-weight homopolyethylene as a matrix, intimately mixed with a high-molecular-weight copolymer that enhances mechanical properties, such as impact strength at low temperatures or stress crack resistance.

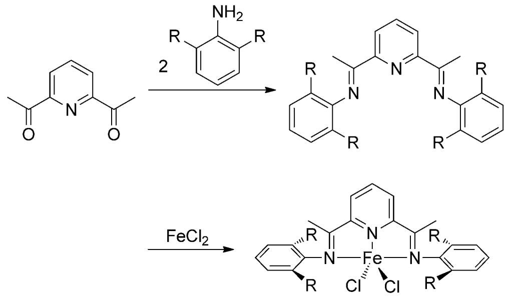

Figure 26. Iron catalyst precursor for linear ethylene polymerization.

12. Catalytic Polymerization to Syndiotactic Polystyrene

Atactic polystyrene obtained by free-radical polymerization is a widely used amorphous plastic with favorable electrical properties as an insulating material, low moisture absorption, and good processability. However, higher-temperature applications are prohibited by its glass transition temperature of 100 °C. Early on, Natta et al. reported the synthesis of crystalline isotactic polystyrene, with a melting point of 240 °C.[200] This polymer did not find commercial

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applications, which was due to its slow rate of crystallization, which makes processing impracticable.

Syndiotactic polystyrene (sPS) was first described in 1985 by Ishihara et al. at Idemitsu Kosan.[201] It has an extraordinarily high melting point of about 270 °C, which is 30 °C higher than for the previously discovered isotactic polystyrene. More importantly, it crystallizes at a reasonably fast rate. Syndiotactic polystyrene was subject to a joint development by Idemitsu and Dow starting from 1988.[202]

Various titanium compounds, such as $TiCl_4$, $Ti(OEt)_4$, $TiBn_4$, $[Cp_2TiCl_2]$, $[CpTiCl_3]$, and $[Cp^*TiCl_3]$, were found to produce syndiotactic polystyrene upon activation with MAO. Some zirconium compounds also showed activity, but this was generally lower than for the titanium compounds, as was the stereoregularity.[203,204] Further investigations showed that the half-sandwich titanium complexes ($[CpTiX_3]$) were the most active and selective catalysts (> 90 % syndiotacticity). In general, electron-donating substituents at the cyclopentadienyl ligand increase the activity. Alkoxides as ligands X, such as OMe, O*i*Pr, or OPh, result in higher activities than chloride and bulky or electron-withdrawing alkoxides.[205] Kaminsky and co-workers discovered that fluoride-coordinated catalyst precursors ($[CpTiF_3]$) afforded higher activities, temperature stability, and polymer molecular weights than the corresponding chlorine-coordinated catalysts, even at low Al/Ti ratios of 300.[206] Further catalysts have been studied extensively by different research groups.[207–209]

Apart from Ti^{IV} catalyst precursors, Ti^{III} compounds also yield highly active catalysts upon activation with MAO.[205,210] This observation leads to the assumption that Ti^{III} is the active species in syndiospecific styrene polymerization, and indeed EPR studies by Chien et al. provided evidence for the formation of a Ti^{III} species during activation with MAO and polymerization.[211] This finding could be further supported by comparison of ethylene and styrene polymerization activities at 0 °C of $[Cp^*TiCl_3]$/MAO with and without ageing of the activated catalyst precursor at 70 °C for 20 min. The aged catalyst was very active in styrene and less active in ethylene polymerization, whereas the unaltered catalyst performed in the opposite way.[212] These findings lead to the conclusion that Ti^{IV} precursors are reduced by MAO or other aluminum alkyls to form a cationic Ti^{III} species, which is active in the syndiospecific polymerization of styrene.[207]

Mechanistic investigations have been carried out to understand the stereoselectivity of this polymerization reaction. NMR studies with partially deuterated styrene revealed a *cis* addition of the growing polymer chain to the double bond of the monomer, from analysis of coupling constants. End group analysis of the polymer chains revealed a 2,1-insertion mechanism into metal–carbon as well as metal–hydride bonds, with β-hydride elimination being a relevant termination pathway. Analysis of stereodefect structures by ^{13}C NMR spectroscopy suggested a chain-end control mechanism for the syndioselective styrene polymerization.[205,207] The selectivity is believed to result from a η^n coordination of the phenyl moiety of the last inserted repeat unit to the metal center, which leads to a fixed conformation of the growing polymer chain (Figure 27).[207,212] This coordination was evidenced by EPR spectroscopy, where a delocalization of the Ti^{III} d^1 electron to the aromatic ring could be observed.[213] Migratory insertion of the η^2 coordinated styrene monomer and substitution of the coordinated phenyl moiety by the newly incorporated monomer unit leads to a mirror-inverted complex.[207]

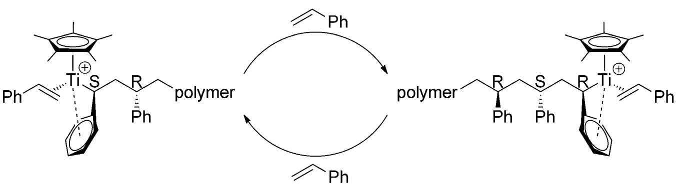

Figure 27. Suggested mechanism for the syndioselective polymerization of styrene.

The upscaling of the polymerization process required a rather specific development. In bulk polymerization, the polymer precipitates already at low conversions, and swelling of the precipitated particles with monomer leads to gelation and significant reactor fouling at higher conversions. Insufficient heat transfer also becomes a problem. Solution polymerization at temperatures where the polymer is dissolved is not feasible owing to catalyst decomposition and loss of stereocontrol. Suspension processes require working in nearly neat monomer to be sufficiently effective. Thus, a continuous fluidized powder-bed polymerization process was developed in which the polymerization occurs on the surface of seeding polymer particles in an average high conversion steady state. Fluidization is achieved mechanically by a double helical agitator operated in upflow mixing mode. Preactivated catalyst and monomer are continuously added to the polymerization reaction and polymer is continuously removed at the bottom of the reactor. New particles are created by mechanically breaking older ones, such that no seeding particles have to be added to the running polymerization reaction. The heat of reaction is removed by evaporation of a low-boiling-point solvent such as pentane, which is continuously added and recondensed, or by evaporation of monomer under reduced pressure (Figure 28).[202,214]

Usually syndiotactic polystyrene is used in the form of glass-fiber-reinforced compounds, which have superior strength compared to the brittle neat sPS. Also nucleating

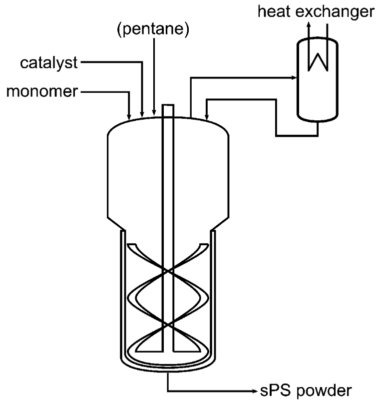

Figure 28. Fluidized powder-bed reactor for syndiotactic polystyrene production.[202]

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agents are frequently added to improve the crystallization rate during processing.[215] Owing to its low dielectric constant and dissipation factor,[216] sPS is applied for electrical connectors, plugs, and sockets or automotive power distribution centers, which have to resist high temperatures. Other applications include high-temperature-resistant consumer articles such as clothes-iron skirts or plastic baking tins.[214]

Syndiotactic polystyrene was commercialized in the 1990s by Idemitsu as Xarec and by Dow under the tradename Questra. However, Dow left this business in 2005.[202]

13. Nickel and Palladium Catalysts for the Preparation of Polynorbornene

Homopolymers and copolymers of cyclic olefins have gained attention owing to their specific properties, such as transparency, low dielectric constant, low optical birefringence, low water absorption, and high-temperature stability. Apart from polyalkenamers generated by ring-opening metathesis polymerization (ROMP), first commercial applications of norbornene type monomers were in the field of ethylene propylene diene monomer (EPDM) rubber production and the copolymerization of ethylene with tetracyclododecene (APEL, Mitsui Chemicals) based on vanadium catalyst technology.[217,218] Later, metallocene catalysts were developed for the insertion copolymerization of cyclic olefins. Topas cycloolefin copolymers (COCs) were developed jointly using metallocene technology by Mitsui and Hoechst. Currently, these materials are available from Topas Advanced Polymers, a joint venture of Daicel and Polyplastics.[219] These polymers contain a large portion of norbornene, up to 50 wt %, and their properties reflect the rigidity of the norbornene-derived bicyclic repeat units which do not crystallize: they possess a high glass-transition temperature that is typically up to 200 °C, and they are amorphous and transparent.

For the vinyl addition homopolymerization of norbornene monomers, electrophilic cationic palladium complexes (for example, $[Pd(NCMe)_4][BF_4]_2$) were studied early on,[220] and many other metal catalysts promote this reaction.[221] Goodall and co-workers at B. F. Goodrich studied norbornene insertion polymerization with cationic nickel and palladium complexes devoid of ligands coordinating via heteroatoms (Figure 29).[217] Such very reactive complexes containing only olefinic and allylic ligands had been studied intensely by Wilke and co-workers, and were termed "naked nickel".[222] Amongst others, they have also been studied for the polymerization of butadiene.[223]

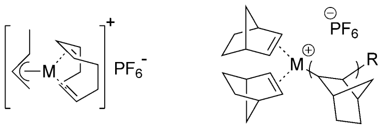

Figure 29. Structure of "naked" nickel and palladium catalysts and proposed active species in norbornene insertion polymerization (M = Ni, Pd).

The complexes can be prepared by oxidative addition of allyl or crotyl halide, respectively, to metal(0) precursors. The resulting halide-bridged dimers are reacted further with halide abstracting agents, such as silver or thallium salts of non-coordinating anions, to yield the cationic complexes.

The nickel complex is a very active catalyst for norbornene homopolymerization, leading to high conversion and high molecular weights in 1,2-dichloroethane solutions within seconds or a few minutes. The resulting polynorbornenes are soluble in hydrocarbons at room temperature, even at molecular weights $> 10^6$ g mol^{-1}, indicating a nonstereoregular structure, which was further confirmed by ^{13}C NMR spectroscopy. The corresponding palladium catalysts are significantly less active and the resulting polymer is insoluble; only low-molecular-weight fractions can be dissolved in hot *o*-dichlorobenzene. ^{13}C NMR spectra indicate a more stereoregular structure of the palladium-catalyzed polynorbornene than for the nickel-derived polymer.[217]

Although catalytic activity of these "naked" transition metal complexes is extremely high, initiation can be relatively slow.[217] NMR studies on related nickel complexes by Brookhart and co-workers indicate that the first norbornene insertion product (Figure 30) is relatively unreactive, resulting in a slow initiation of the polymerization reaction.[224]

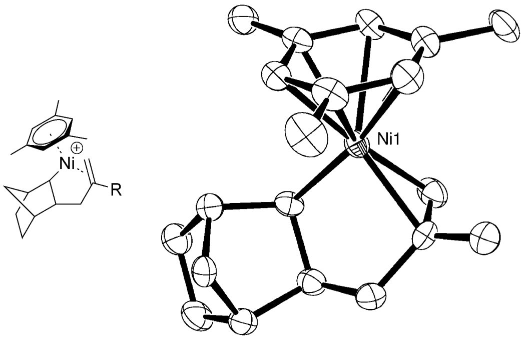

Figure 30. First insertion product in the "naked"-nickel-catalyzed norbornene polymerization.[224]

Copolymerization of norbornene with ethylene or 1-olefins is not possible with these catalysts owing to rapid β-hydride elimination after 1-olefin enchainment, a chain-transfer step that is highly disfavored in norbornene homopolymerization. This propensity for chain transfer after a 1-olefin insertion can be utilized for molecular-weight control in the Ni^{II}-catalyzed synthesis of polynorbornenes, by addition of small amounts of 1-olefins, such as 1-decene, as chain-transfer agents. For the palladium system almost no effect is observed, most likely because insertion of 1-olefins cannot compete with norbornene enchainment.[217]

The atactic norbornene homopolymers possess a glass-transition temperature of 370 to 390 °C, which makes melt processing impractical. Shaped parts from these polymers can be generated by reaction injection molding, where polymerization occurs in a mold to directly form a shaped part.[225] Melt processability can be achieved by tailoring the glass-

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transition temperature by copolymerization of 5-alkylnorbornenes.[217]

Apart from the aforementioned single-component catalysts, more conveniently accessible in situ catalyst systems have been studied. The combination of $Ni(O_2CR)_2/HSbF_6/BF_3{\cdot}Et_2O/AlEt_3$ (R = 2-ethylhexyl; Ni:Sb:B:Al = 1:1:9:10) yielded an in situ catalyst which exhibits an activity similar to the single-component "naked" nickel catalyst.[217] Applying $B(C_6F_5)_3$ in the in situ catalyst system results in transfer of C_6F_5 groups to the metal. The resulting complex, $[(\eta^6\text{-tolyl})Ni(C_6F_5)_2]$[226] (Figure 31), is presumed to polymerize norbornene by insertion into an Ni-aryl σ-bond while the other C_6F_5 group stays bound to the metal. ^{13}C NMR spectroscopy revealed a microstructure completely different from the polynorbornene obtained by the "naked" nickel catalyst. Furthermore, the tolerance toward polar-group-functionalized monomers is enhanced, presumably by the C_6F_5 group remaining on the metal. Molecular-weight control by 1-olefins as chain-transfer agents is not feasible in this case, as the $[NiH(C_6F_5)]$ species formed undergoes reductive elimination to C_6F_5H and Ni^0.[217,227]

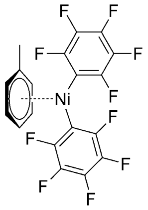

Figure 31. Structure of $[(\eta^6\text{-tolyl})Ni(C_6F_5)_2]$.

An addition of phosphines, such as PCy_3 or $P(o\text{-}Tol)_3$, to the palladium catalysts strongly enhanced polymerization activity; more than 10^5 moles of norbornene can be converted per mole of palladium. Further, the temperature stability of the catalysts increased to 60–100 °C compared to 20–30 °C for the "naked" catalyst systems. These catalysts possess a higher functional-group tolerance and can even be employed in aqueous systems.[217,228–230]

Insertion-polymerized polynorbornenes were commercialized by B. F. Goodrich and are now available from Promerus LLC, a subsidiary of Sumitomo Bakelite. These amorphous, transparent, high-T_g polynorbornene derivatives are marketed for electronics applications in packaging (Avatrel), as photoresists, and others.[217]

14. Conclusions

Like industrial large scale catalytic syntheses of small molecules, polymerization is dominated by heterogeneous catalysis, albeit for different reasons: modern heterogeneous Ziegler catalysts are not only extremely active and stereoselective, but they also control the product morphology. Nonetheless, single-site polymerization catalysts, and specifically the "post-metallocene" catalysts considered herein, have advanced to sizeable industrial applications. In terms of scale, some of these applications correspond with the large homogeneous catalytic processes for small-molecule synthesis.

Heterogenization of single site catalysts on solid supports is often accompanied by compromises in activity and selectivity, as already precedented by metallocene-catalyzed polymerizations. In this context, it is notable that supported "post-metallocene" catalysts can meet the stringent requirements of industrial processes as exemplified by utilization of zirconium or iron complexes in the production of bimodal polyethylenes. Nonetheless, a large part of the industrial applications of "post-metallocene" polymerization catalysis indeed employ solution processes. In several instances these are carried out at high temperatures (≥ 140 °C) to keep the products soluble in the reaction solvent and to reduce the viscosity of the reaction mixture. This requires sufficiently temperature-stable catalysts. Many of the catalyst systems reviewed show how this can be achieved by appropriate ligand coordination environments.

The catalytic polymerizations reviewed herein also illustrate how an appropriate non-metallocene ligand environment can enable desirable polymer microstructures, for example by an incorporation also of bulky comonomers. The potential of tuning the catalytic properties of different metal centers by their well-defined ligand environment is also well-illustrated by chain-shuttling polymerization. This elegant concept affords otherwise inaccessible blockcopolymer microstructures from simple olefinic monomers, and expands the scope of polyolefins applications. Notably, stereoregular polymerization and particularly enantiomorphic site control are not very prominent in terms of practical utilization of "post-metallocene" catalysts.

Non-metallocene metal complexes in the context of polymerization catalysis offer a rich and fascinating coordination chemistry, unique mechanistic features, and novel polymer microstructures. Beyond these fundamental aspects, however, given the many difficult and often unexpected, sometimes seemingly trivial hurdles that must be overcome to take basic research to industrial processes and commercially successful materials, it is remarkable that this chemistry is also applied practically in many instances.

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[1] W. Kaminsky, K. Külper, H. H. Brintzinger, F. R. W. P. Wild, *Angew. Chem.* **1985**, *97*, 507 – 508; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 507 – 508.
[2] H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem.* **1995**, *107*, 1255 – 1283; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143 – 1170.
[3] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448 – 468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428 – 447.
[4] V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283 – 316.
[5] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169 – 1204.
[6] K. P. Bryliakov, *Russ. Chem. Rev.* **2007**, *76*, 253 – 277.
[7] Polyolefins Planning Service: Executive Report, Global Commercial Analysis 2009; ChemSystems, April 2010.
[8] A. H. Tullo, *Chem. Eng. News* **2010**, *88(42)*, 10 – 16.
[9] E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391 – 1434.
[10] F. Rix, (Exxon), WO 0130785, **2001**.
[11] R. K. Rosen, D. D. Vanderlende, (Dow), WO 9735893, **1997**.
[12] J. F. Walzer, Jr., (Exxon), US 5643847, **1997**.

[13] E. M. Carnahan, M. J. Carney, D. R. Neithamer, P. N. Nickias, K.-Y. Shih, L. Spencer, (Dow Chemical Co., W. R. Grace), WO 9719959, **1997**.

[14] L. Luo, X. Wu, S. P. Diefenbach, (Albemarle), WO 2008076632, **2008**.

[15] Y. Sun, M. V. Metz, C. L. Stern, T. J. Marks, *Organometallics* **2000**, *19*, 1625–1627.

[16] N. Millot, S. Soignier, C. C. Santini, A. Baudouin, J.-M. Basset, *J. Am. Chem. Soc.* **2006**, *128*, 9361–9370.

[17] N. Popoff, R. M. Gauvin, A. De Mallmann, M. Taoufik, *Organometallics* **2012**, *31*, 4763–4768.

[18] J. Klosin, G. R. Roof, E. Y.-X. Chen, K. A. Abboud, *Organometallics* **2000**, *19*, 4684–4686.

[19] J. Klosin, (Dow Chemical Co.), WO 2000011006, **2000**.

[20] K. P. Bryliakov, E. P. Talsi, M. Bochmann, *Organometallics* **2004**, *23*, 149–152.

[21] D. E. Babushkin, H.-H. Brintzinger, *J. Am. Chem. Soc.* **2002**, *124*, 12869–12873.

[22] P. D. Bolton, E. Clot, A. R. Cowley, P. Mountford, *J. Am. Chem. Soc.* **2006**, *128*, 15005–15018.

[23] S. A. Sangokoya, S. P. Diefenbach, C. Daly, L. S. Simeral, (Albemarle), WO 2007005400, **2007**.

[24] L. Luo, S. A. Sangokoya, X. Wu, S. P. Diefenbach, B. Kneale, (Albemarle), WO 2009029857, **2009**.

[25] L. Luo, X. Wu, S. P. Diefenbach, (Albemarle), WO 2012122332, **2012**.

[26] V. Busico, R. Cipullo, F. Cutillo, N. Friederichs, S. Ronca, B. Wang, *J. Am. Chem. Soc.* **2003**, *125*, 12402–12403.

[27] V. C. Williams, C. Dai, Z. Li, S. Collins, W. E. Piers, W. Clegg, M. R. J. Elsegood, T. B. Marder, *Angew. Chem.* **1999**, *111*, 3922–3926; *Angew. Chem. Int. Ed.* **1999**, *38*, 3695–3698.

[28] R. Sugimoto, T. Iwatani, K. Takeuchi, (Mitsui), JP 06136053, **1992**.

[29] R. A. Stapleton, B. R. Galan, S. Collins, R. S. Simons, J. C. Garrison, W. J. Youngs, *J. Am. Chem. Soc.* **2003**, *125*, 9246–9247.

[30] J. S. J. McCahill, G. C. Welch, D. W. Stephan, *Dalton Trans.* **2009**, 8555–8561.

[31] A. L. McKnight, R. M. Waymouth, *Chem. Rev.* **1998**, *98*, 2587–2598.

[32] H. Braunschweig, F. M. Breitling, *Coord. Chem. Rev.* **2006**, *250*, 2691–2720.

[33] P. J. Shapiro, E. Bunel, W. P. Schaefer, J. E. Bercaw, *Organometallics* **1990**, *9*, 867–869.

[34] J. Okuda, *Chem. Ber.* **1990**, *123*, 1649–1651.

[35] J. C. Stevens, F. J. Timmers, D. R. Wilson, G. F. Schmidt, P. N. Nickias, R. K. Rosen, G. W. Knight, S.-Y. Lai, (Dow Chemical Co., USA), EP 0 416 815 A2, **1991**.

[36] a) J. A. M. Canich, (Exxon Chemical, Inc., USA), US 5 026 798, **1991**; b) J. A. M. Canich, (Exxon Chemical, Inc., USA), EP 0 420 436 A1, **1991**; c) J. A. M. Canich, G. F. Licciardi, (Exxon Chemical, Inc., USA), US 5 057 475, **1991**.

[37] J. C. Stevens, *Stud. Surf. Sci. Catal.* **1994**, *89*, 277–284.

[38] a) G. A. Luinstra, J. H. Teuben, *J. Chem. Soc. Chem. Commun.* **1990**, 1470–1471; b) F. Amor, J. Okuda, *J. Organomet. Chem.* **1996**, *520*, 245–248.

[39] D. D. Devore, (Dow Chemical Co., USA), EP 0 514 828 A1, **1992**.

[40] J. Cano, K. Kunz, *J. Organomet. Chem.* **2007**, *692*, 4411–4423.

[41] a) J. C. Stevens, *Stud. Surf. Sci. Catal.* **1996**, *101*, 11–20; b) R. E. LaPointe, J. C. Stevens, P. N. Nickias, M. H. McAdon, (Dow Chemical, USA), EP 0 520 732 B1, **1992**.

[42] a) J. Klosin, W. J. Kruper, Jr., P. N. Nickias, G. R. Roof, P. De Waele, K. A. Abboud, *Organometallics* **2001**, *20*, 2663–2665; b) J. Klosin, W. J. Kruper, Jr., P. N. Nickias, J. T. Patton, D. R. Wilson, (Dow Chemical, USA), EP 0 923 589 B1, **1997**.

[43] L. J. Irwin, J. H. Reibenspies, S. A. Miller, *J. Am. Chem. Soc.* **2004**, *126*, 16716–16717.

[44] L. J. Irwin, S. A. Miller, *J. Am. Chem. Soc.* **2005**, *127*, 9972–9973.

[45] a) BP/Dow. Technology co-operation for licensing metallocenes in gas phase process. Press release of Aug. 5, **1996**; b) *BP Frontiers Magazine*, September **2001**, 17–20; c) INEOS Eltex PF product brochure; d) INEOS Eltex TUB 220-RT product brochure.

[46] DuPont Dow Elastomers. DuPont plans EPDM output. Press release of Aug. 24, **1998**.

[47] a) S. L. Martin, L. C. Cady, D. P. Denton, D. L. Ramage, *ACS Rubber Division Technical Papers* **2002**, 262–278; b) M. S. Edmondson, *Rubber World*, November **2008**.

[48] Dow. Dow closings to include EPDM plant. Press release of Dec. 10, **2008**.

[49] P. S. Chum, K. W. Swogger, *Prog. Polym. Sci.* **2008**, *33*, 797–819.

[50] P. S. Chum, W. J. Kruper, M. J. Guest, *Adv. Mater.* **2000**, *12*, 1759–1767.

[51] K. Soga, T. Uozumi, S. Nakamura, T. Toneri, T. Teranishi, T. Sano, T. Arai, T. Shiono, *Macromol. Chem. Phys.* **1996**, *197*, 4237–4251.

[52] W.-J. Wang, D. Yan, S. Zhu, A. E. Hamielec, *Macromolecules* **1998**, *31*, 8677–8683.

[53] T. K. Woo, P. M. Margl, T. Ziegler, P. E. Blöchl, *Organometallics* **1997**, *16*, 3454–3468.

[54] J. Wang, H. Li, N. Guo, L. Li, C. L. Stern, T. J. Marks, *Organometallics* **2004**, *23*, 5112–5114.

[55] M. Delferro, T. J. Marks, *Chem. Rev.* **2011**, *111*, 2450–2485.

[56] H. Li, T. J. Marks, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15295–15302.

[57] L. Li, M. V. Metz, H. Li, M.-C. Chen, T. J. Marks, L. Liable-Sands, A. L. Rheingold, *J. Am. Chem. Soc.* **2002**, *124*, 12725–12741.

[58] F. G. Sernetz, R. Mülhaupt, R. M. Waymouth, *Macromol. Chem. Phys.* **1996**, *197*, 1071–1083.

[59] D. J. Arriola, M. Bokota, R. E. Campbell, Jr., J. Klosin, R. E. LaPointe, O. D. Redwine, R. B. Shankar, F. J. Timmers, K. A. Abboud, *J. Am. Chem. Soc.* **2007**, *129*, 7065–7076.

[60] a) N. Guo, L. Li, T. J. Marks, *J. Am. Chem. Soc.* **2004**, *126*, 6542–6543; b) N. Guo, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **2008**, *130*, 2246–2261.

[61] Dow. ESI production ends: Dow rethinks uses. Press release of July 12, **2002**.

[62] G.-J. M. Gruter in *Metallocene Technology: a one-day seminar*; Rapra Technology Limited, **1997**, Paper 3.

[63] a) J. A. M. van Beek, G. H. J. van Doremaele, G. J. M. Gruter, H. J. Arts, G. H. M. R. Eggels, (DSM), WO 96/13529, **1996**; b) G. J. M. Gruter, M. Kranenburg, M. Herklots, (DSM), EP 0 919 571 A1, **1997**.

[64] R. E. v. H. Spence, X. Gao, L. Koch, S. J. Brown, D. G. Harrison, (Nova Chemicals), US 6 124 487, **1998**.

[65] H. Katayama, M. Nabika, A. Imai, A. Miyashita, T. Watanabe, H. Johohji, Y. Oda, H. Hanaoka, (Sumitomo Chemical Company), EP 0 842 939 B1, **1996**.

[66] M. Nabika, H. Katayama, T. Watanabe, H. Kawamura-Kuribayashi, K. Yanagi, A. Imai, *Organometallics* **2009**, *28*, 3785–3792.

[67] T. Senda, H. Hanaoka, T. Hino, Y. Oda, H. Tsurugi, K. Mashima, *Macromolecules* **2009**, *42*, 8006–8009.

[68] T. Senda, H. Hanaoka, Y. Okado, Y. Oda, H. Tsurugi, K. Mashima, *Organometallics* **2009**, *28*, 6915–6926.

[69] T. Senda, H. Hanaoka, S. Nakahara, Y. Oda, H. Tsurugi, K. Mashima, *Macromolecules* **2010**, *43*, 2299–2306.

[70] T. V. Lubben, P. T. Wolczanski, G. D. Van Duyne, *Organometallics* **1984**, *3*, 977–983.

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[71] a) S. Anfang, K. Harms, F. Weller, O. Borgmeier, H. Lueken, H. Schilder, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1998**, *624*, 159–166; b) T. Rübenstahl, F. Weller, S. Wocadlo, W. Massa, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1995**, *621*, 953–958.

[72] D. W. Stephan, *Organometallics* **2005**, *24*, 2548–2560.

[73] D. W. Stephan, J. C. Stewart, F. Guérin, R. E. v. H. Spence, W. Xu, D. G. Harrison, *Organometallics* **1999**, *18*, 1116–1118.

[74] a) K. Dehnicke, F. Weller, *Coord. Chem. Rev.* **1997**, *158*, 103–169; b) K. Dehnicke, M. Krieger, W. Massa, *Coord. Chem. Rev.* **1999**, *182*, 19–65.

[75] H. Staudinger, J. Meyer, *Helv. Chim. Acta* **1919**, *2*, 635–646.

[76] D. W. Stephan, J. C. Stewart, F. Guérin, S. Courtenay, J. Kickham, E. Hollink, C. Beddie, A. Hoskin, T. Graham, P. Wei, R. E. v. H. Spence, W. Xu, L. Koch, X. Gao, D. G. Harrison, *Organometallics* **2003**, *22*, 1937–1947.

[77] D. W. Stephan, *Macromol. Symp.* **2001**, *173*, 105–116.

[78] a) J. E. Kickham, F. Guérin, J. C. Stewart, D. W. Stephan, *Angew. Chem.* **2000**, *112*, 3406–3409; *Angew. Chem. Int. Ed.* **2000**, *39*, 3263–3266; b) J. E. Kickham, F. Guérin, J. C. Stewart, E. Urbanska, D. W. Stephan, *Organometallics* **2001**, *20*, 1175–1182.

[79] D. W. Stephan, F. Guérin, R. E. v. H. Spence, L. Koch, X. Gao, S. J. Brown, J. W. Swabey, Q. Wang, W. Xu, P. Zoricak, D. G. Harrison, *Organometallics* **1999**, *18*, 2046–2048.

[80] F. Guérin, J. C. Stewart, C. Beddie, D. W. Stephan, *Organometallics* **2000**, *19*, 2994–3000.

[81] J. E. Kickham, F. Guérin, D. W. Stephan, *J. Am. Chem. Soc.* **2002**, *124*, 11486–11494.

[82] C. Baar, S. Brown, P. Zoricak, Commercial Development of Single-Site Catalyst Technologies for Polyethylene Production, **2005**, Presentation by Nova Chemicals Corporation.

[83] a) N. Yue, E. Hollink, F. Guérin, D. W. Stephan, *Organometallics* **2001**, *20*, 4424–4433; b) E. Hollink, P. Wei, D. W. Stephan, *Organometallics* **2004**, *23*, 1562–1569.

[84] N. L. S. Yue, D. W. Stephan, *Organometallics* **2001**, *20*, 2303–2308.

[85] E. Hollink, J. C. Stewart, P. Wei, D. W. Stephan, *Dalton Trans.* **2003**, 3968–3974.

[86] E. Hollink, P. Wei, D. W. Stephan, *Can. J. Chem.* **2004**, *82*, 1304–1313.

[87] C. Beddie, E. Hollink, P. Wei, J. Gauld, D. W. Stephan, *Organometallics* **2004**, *23*, 5240–5251.

[88] J. McMeeking, X. Gao, R. E. v. H. Spence, S. J. Brown, D. Jeremic, (Nova Chemicals), WO 99/14250, **1999**.

[89] M. J. Ferreira, A. M. Martins, *Coord. Chem. Rev.* **2006**, *250*, 118–132.

[90] A. R. Dias, M. T. Duarte, A. C. Fernandes, S. Fernandes, M. M. Marques, A. M. Martins, J. F. da Silva, S. S. Rodrigues, *J. Organomet. Chem.* **2004**, *689*, 203–213.

[91] K. Nomura, K. Fujita, M. Fujiki, *J. Mol. Catal. A* **2004**, *220*, 133–144.

[92] K. Nomura, J. Liu, *Dalton Trans.* **2011**, *40*, 7666–7682.

[93] H. Zhang, K. Nomura, *J. Am. Chem. Soc.* **2005**, *127*, 9364–9365.

[94] a) DSM Elastomers. DSM continues to invest in innovative growth in performance materials cluster. Press release of March 27, **2007**; b) A. Leblanc, M. A. Zuideveld, V. Quiroga, E. Ijpei, E. Arts, G. van Doremaele, 3rd Blue Sky Conference on Catalytic Olefin Polymerization, **2010**, P43; c) V. Quiroga, A. Leblanc, M. A. Zuideveld, E. Ijpeij, E. Arts, G. van Doremaele, 3rd Blue Sky Conference on Catalytic Olefin Polymerization, **2010**, P62; d) M. A. Zuideveld, B. Coussens, E. Ijpeij, E. Arts, A. Leblanc, V. Quiroga, G. van Doremaele, 3rd Blue Sky Conference on Catalytic Olefin Polymerization, **2010**, P92.

[95] E. G. Ijpeij, B. Coussens, M. A. Zuideveld, G. H. J. van Doremaele, P. Mountford, M. Lutz, A. L. Spek, *Chem. Commun.* **2010**, *46*, 3339–3341.

[96] a) E. G. Ijpeij, P. J. H. Windmuller, H. J. Arts, F. van der Burgt, G. H. J. van Doremaele, M. A. Zuideveld, (DSM), WO 2005/090418 A1, **2005**; b) P. J. H. Windmuller, G. H. J. van Doremaele, (DSM), WO 2005/005496 A2, **2005**; c) E. G. Ijpeij, M. A. Zuideveld, H. J. Arts, F. van der Burgt, G. H. J. van Doremaele, (DSM), WO 2007/031295 A1, **2007**.

[97] a) W. P. Kretschmer, C. Dijkhuis, A. Meetsma, B. Hessen, J. H. Teuben, *Chem. Commun.* **2002**, 608–609; b) W. P. Kretschmer, (Stichting Dutch Polymer Institute), EP 1 373 332 B1, **2002**.

[98] G. H. J. van Doremaele, M. A. Zuideveld, A. Leblanc, V. F. Quiroga Norambuena, (DSM), EP 2 319 874 A1, **2009**.

[99] M. Dees, M. van Duin, C. Twigg, H. Dikland, *Rubber World* **2009**, *240*, 13–24.

[100] a) Lanxess. LANXESS to acquire DSM Elastomers. Press release of Dec. 14, **2010**; b) Lanxess. LANXESS completes acquisition of DSM Elastomers. Press release of May 3, **2011**.

[101] Lanxess. LANXESS successfully completes conversion to ACE technology at Geleen EPDM site. Press release of July 1, **2013**.

[102] Lanxess. LANXESS to build world's largest EPDM plant in China. Press release of Sept. 5, **2012**.

[103] J. D. Scollard, D. H. McConville, N. C. Payne, J. J. Vittal, *Macromolecules* **1996**, *29*, 5241–5243.

[104] J. D. Scollard, D. H. McConville, *J. Am. Chem. Soc.* **1996**, *118*, 10008–10009.

[105] L.-C. Liang, R. R. Schrock, W. M. Davis, D. H. McConville, *J. Am. Chem. Soc.* **1999**, *121*, 5797–5798.

[106] a) R. R. Schrock, A. L. Casado, J. T. Goodman, L.-C. Liang, P. J. Bonitatebus, Jr., W. M. Davis, *Organometallics* **2000**, *19*, 5325–5341; b) R. R. Schrock, P. J. Bonitatebus, Jr., Y. Schrodi, *Organometallics* **2001**, *20*, 1056–1058; c) Y. Schrodi, R. R. Schrock, P. J. Bonitatebus, Jr., *Organometallics* **2001**, *20*, 3560–3573.

[107] D. H. McConville, R. R. Schrock, (Univation Technologies, Massachusetts Institute of Technology), WO 00/69922, **2000**.

[108] H.-T. Liu, C. R. Mure, (Univation Technologies), WO 2010/008964 A1, **2010**.

[109] a) D. H. McConville, D. R. Loveday, M. W. Holtcamp, J. F. Szul, K. A. Erickson, S. Mawson, T. H. Kwack, F. J. Karol, D. J. Schreck, M. G. Goode, P. T. Daniell, M. G. McKee, C. C. Williams, (Univation Technologies), WO 01/30861 A1, **2001**; b) T. H. Kwalk, (Univation Technologies), US 2006/0036041 A1, **2006**.

[110] I. Burdett, *Hydrocarbon Eng.* **2008**, *13(6)*, 67–76.

[111] S.-C. Kao, F. C. Rix, D. Li, C. J. Harlan, P. A. Khokhani, (Univation Technologies), WO 2010/132811 A1, **2010**.

[112] a) R. E. Murray, (Union Carbide), US 6 096 676, **2000**; b) R. E. Murray, (Univation Technologies), WO 03/051935 A1, **2003**; c) R. E. Murray, A. M. Harrison, (Univation Technologies), US 7 199 255 B2, **2007**.

[113] P. De Waele, B. A. Jazdzewski, J. Klosin, R. E. Murray, C. N. Theriault, P. C. Vosejpka, J. L. Petersen, *Organometallics* **2007**, *26*, 3896–3899.

[114] H. Tsurugi, R. Ohnishi, H. Kaneko, T. K. Panda, K. Mashima, *Organometallics* **2009**, *28*, 680–687.

[115] R. D. J. Froese, B. A. Jazdzewski, J. Klosin, R. L. Kuhlman, C. N. Theriault, D. M. Welsh, K. A. Abboud, *Organometallics* **2011**, *30*, 251–262.

[116] a) R. Figueroa, R. D. Froese, Y. He, J. Klosin, C. N. Theriault, K. A. Abboud, *Organometallics* **2011**, *30*, 1695–1709; b) P. P. Fontaine, R. Figueroa, S. D. McCann, D. Mort, J. Klosin, *Organometallics* **2013**, *32*, 2963–2972.

[117] T. R. Boussie, G. M. Diamond, C. Goh, K. A. Hall, A. M. LaPointe, M. K. Leclerc, V. Murphy, J. A. W. Shoemaker, H. Turner, R. K. Rosen, J. C. Stevens, F. Alfano, V. Busico, R. Cipullo, G. Talarico, *Angew. Chem.* **2006**, *118*, 3356–3361; *Angew. Chem. Int. Ed.* **2006**, *45*, 3278–3283.

[118] T. R. Boussie, G. M. Diamond, C. Goh, K. A. Hall, A. M. LaPointe, M. Leclerc, C. Lund, V. Murphy, J. A. W. Shoemaker, U. Tracht, H. Turner, J. Zhang, T. Uno, R. K. Rosen, J. C. Stevens, *J. Am. Chem. Soc.* **2003**, *125*, 4306 – 4317.

[119] G. J. Domski, E. B. Lobkovsky, G. W. Coates, *Macromolecules* **2007**, *40*, 3510 – 3513.

[120] R. D. J. Froese, P. D. Hustad, R. L. Kuhlman, T. T. Wenzel, *J. Am. Chem. Soc.* **2007**, *129*, 7831 – 7840.

[121] C. Zuccaccia, V. Busico, R. Cipullo, G. Talarico, R. D. J. Froese, P. C. Vosejpka, P. D. Hustad, A. Macchioni, *Organometallics* **2009**, *28*, 5445 – 5458.

[122] C. Zuccaccia, A. Macchioni, V. Busico, R. Cipullo, G. Talarico, F. Alfano, H. W. Boone, K. A. Frazier, P. D. Hustad, J. C. Stevens, P. C. Vosejpka, K. A. Abboud, *J. Am. Chem. Soc.* **2008**, *130*, 10354 – 10368.

[123] V. Busico, R. Cipullo, R. Pellecchia, L. Rongo, G. Talarico, A. Macchioni, C. Zuccaccia, R. D. J. Froese, P. D. Hustad, *Macromolecules* **2009**, *42*, 4369 – 4373.

[124] http://www.dow.com/elastomers/products/versify.htm,accessed July 18, 2014.

[125] P. G. Cozzi, E. Gallo, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *Organometallics* **1995**, *14*, 4994 – 4996.

[126] H. Makio, H. Terao, A. Iwashita, T. Fujita, *Chem. Rev.* **2011**, *111*, 2363 – 2449.

[127] T. Fujita, Y. Thoi, M. Mitani, S. Matsui, J. Saito, M. Nitabaru, K. Sugi, H. Makio, T. Tsutsui, (Mitsui Chemicals), EP 0 874 005 B1, **1997**.

[128] S. Matsui, T. Fujita, *Catal. Today* **2001**, *66*, 63 – 73.

[129] H. Makio, N. Kashiwa, T. Fujita, *Adv. Synth. Catal.* **2002**, *344*, 477 – 493.

[130] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* **2001**, *123*, 6847 – 6856.

[131] a) J. Saito, M. Mitani, J.-i. Mohri, Y. Yoshida, S. Matsui, S.-i. Ishii, S.-i. Kojoh, N. Kashiwa, T. Fujita, *Angew. Chem.* **2001**, *113*, 3002 – 3004; *Angew. Chem. Int. Ed.* **2001**, *40*, 2918 – 2920; b) M. Mitani, J.-i. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S.-i. Kojoh, T. Matsugi, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* **2002**, *124*, 3327 – 3336.

[132] a) J. Tian, G. W. Coates, *Angew. Chem.* **2000**, *112*, 3772 – 3775; *Angew. Chem. Int. Ed.* **2000**, *39*, 3626 – 3629; b) J. Tian, P. D. Hustad, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 5134 – 5135.

[133] a) E. Talsi, K. P. Bryliakov, *Top. Catal.* **2013**, *56*, 914 – 922; b) A. Iwashita, M. C. W. Chan, H. Makio, T. Fujita, *Catal. Sci. Technol.* **2014**, *4*, 599 – 610.

[134] G. Talarico, V. Busico, L. Cavallo, *Organometallics* **2004**, *23*, 5989 – 5993.

[135] S.-M. Yu, S. Mecking, *J. Am. Chem. Soc.* **2008**, *130*, 13204 – 13205.

[136] a) K. P. Bryliakov, E. P. Talsi, H. M. Möller, M. C. Baier, S. Mecking, *Organometallics* **2010**, *29*, 4428 – 4430; b) H. M. Möller, M. C. Baier, S. Mecking, E. P. Talsi, K. P. Bryliakov, *Chem. Eur. J.* **2012**, *18*, 848 – 856.

[137] A. Sakuma, M.-S. Weiser, T. Fujita, *Polym. J.* **2007**, *39*, 193 – 207.

[138] G. Milano, L. Cavallo, G. Guerra, *J. Am. Chem. Soc.* **2002**, *124*, 13368 – 13369.

[139] P. Corradini, G. Guerra, L. Cavallo, *Acc. Chem. Res.* **2004**, *37*, 231 – 241.

[140] A. V. Prasad, H. Makio, J. Saito, M. Onda, T. Fujita, *Chem. Lett.* **2004**, *33*, 250 – 251.

[141] H. Makio, T. Fujita, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 52 – 66.

[142] J. B. Edson, Z. Wang, E. J. Kramer, G. W. Coates, *J. Am. Chem. Soc.* **2008**, *130*, 4968 – 4977.

[143] E. Y. Tshuva, I. Goldberg, M. Kol, *J. Am. Chem. Soc.* **2000**, *122*, 10706 – 10707.

[144] A. Cohen, J. Kopilov, M. Lamberti, V. Venditto, M. Kol, *Macromolecules* **2010**, *43*, 1689 – 1691.

[145] K. Press, A. Cohen, I. Goldberg, V. Venditto, M. Mazzeo, M. Kol, *Angew. Chem.* **2011**, *123*, 3591 – 3594; *Angew. Chem. Int. Ed.* **2011**, *50*, 3529 – 3532.

[146] J. Saito, M. Mitani, S. Matsui, N. Kashiwa, T. Fujita, *Macromol. Rapid Commun.* **2000**, *21*, 1333 – 1336.

[147] J. Saito, Y. Suzuki, H. Makio, H. Tanaka, M. Onda, T. Fujita, *Macromolecules* **2006**, *39*, 4023 – 4031.

[148] W.-Q. Hu, X.-L. Sun, C. Wang, Y. Gao, Y. Tang, L.-P. Shi, W. Xia, J. Sun, H.-L. Dai, X.-Q. Li, X.-L. Yao, X.-R. Wang, *Organometallics* **2004**, *23*, 1684 – 1688.

[149] X.-H. Yang, C.-R. Liu, C. Wang, X.-L. Sun, Y.-H. Guo, X.-K. Wang, Z. Wang, Z. Xie, Y. Tang, *Angew. Chem.* **2009**, *121*, 8243 – 8246; *Angew. Chem. Int. Ed.* **2009**, *48*, 8099 – 8102.

[150] G. G. Hlatky, *Chem. Rev.* **2000**, *100*, 1347 – 1376.

[151] Y. Nakayama, J. Saito, H. Bando, T. Fujita, *Chem. Eur. J.* **2006**, *12*, 7546 – 7556.

[152] H. Makio, T. Ochiai, J.-i. Mohri, K. Takeda, T. Shimazaki, Y. Usui, S. Matsuura, T. Fujita, *J. Am. Chem. Soc.* **2013**, *135*, 8177 – 8180.

[153] H. Makio, T. Fujita, *Acc. Chem. Res.* **2009**, *42*, 1532 – 1544.

[154] Mitsui will use the PI catalyst production HDPE. News article on ourchemical.com. Oct. 18, **2011**. Accessed July 24, 2013.

[155] S. Rastogi, D. R. Lippits, G. W. M. Peters, R. Graf, Y. Yao, H. W. Spiess, *Nat. Mater.* **2005**, *4*, 635 – 641.

[156] S. E. Rastogi, K. Garkhail, R. Duchateau, G. J. M. Gruter, D. R. Lippits, (Stichting Dutch Polymer Institute), US 7 671 159 B2, **2010**.

[157] S. Rastogi, Y. Yao, S. Ronca, J. Bos, J. van der Eem, *Macromolecules* **2011**, *44*, 5558 – 5568.

[158] Y. Suzuki, S. Kinoshita, A. Shibahara, S. Ishii, K. Kawamura, Y. Inoue, T. Fujita, *Organometallics* **2010**, *29*, 2394 – 2396.

[159] A. Sattler, J. A. Labinger, J. E. Bercaw, *Organometallics* **2013**, *32*, 6899 – 6902.

[160] I. E. Soshnikov, N. V. Semikolenova, J. Ma, K.-Q. Zhao, V. A. Zakharov, K. P. Bryliakov, C. Redshaw, E. P. Talsi, *Organometallics* **2014**, *33*, 1431 – 1439.

[161] a) *The Catalyst Review* **2011**, *24(4)*, 6; b) Mitsui Chemicals. Mitsui Chemicals to Develop a Highly Active Catalyst for 1-Hexene Production. Press release of June 23, **2008**; c) Mitsui Chemicals. Mitsui Chemicals to Strengthen Added-Value Ethylene Derivative Products of Ichihara Works. Press release of Jan. 30, **2009**.

[162] a) D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman, T. T. Wenzel, *Science* **2006**, *312*, 714 – 719; b) P. D. Hustad, R. L. Kuhlman, D. J. Arriola, E. M. Carnahan, T. T. Wenzel, *Macromolecules* **2007**, *40*, 7061 – 7064; c) P. D. Hustad, R. L. Kuhlman, E. M. Carnahan, T. T. Wenzel, D. J. Arriola, *Macromolecules* **2008**, *41*, 4081 – 4089; d) T. T. Wenzel, D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman, *Topics in Organometallic Chemistry*, *Vol. 26* (Ed.: Z. Guan), Springer, Berlin/Heidelberg, **2009**, pp. 65 – 104.

[163] D. J. Arriola, E. M. Carnahan, Y. W. Cheung, D. D. Devore, D. D. Graf, P. D. Hustad, R. L. Kuhlman, C. Li Pi Shan, B. C. Poon, G. R. Roof, J. C. Stevens, P. J. Stirn, T. T. Wenzel, (Dow Global Technologies), WO 2005/090427 A2, **2005**.

[164] Mitsui Chemicals. Joint Research Agreement with the Dow Chemical Company. Press release of June 21, **2006**.

[165] Dow. Dow Introduces Breakthrough Technology for Effectively Combining PE and PP. Press release of Oct. 17, **2013**.

[166] a) T. T. Wenzel, T. P. Clark, D. R. Wilson, S. B. Klamo, D. J. Arriola, C. N. Theriault, R. D. Froese, (Dow Global Technologies), WO 2012/061706 A1, **2012**; b) T. P. Clark, N. E. Kamber, S. B. Klamo, P. D. Hustad, D. R. Wilson (Dow Chemical, USA), US 2011/0028657 A1, **2011**.

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[167] R. L. Kuhlman, J. Klosin, *Macromolecules* **2010**, *43*, 7903–7904.

[168] a) R. Kempe, *Chem. Eur. J.* **2007**, *13*, 2764–2773; b) L. R. Sita, *Angew. Chem.* **2009**, *121*, 2500–2508; *Angew. Chem. Int. Ed.* **2009**, *48*, 2464–2472; c) J. Mazzolini, E. Espinosa, F. D'Agosto, C. Boisson, *Polym. Chem.* **2010**, *1*, 793–800.

[169] J. Wei, W. Zhang, R. Wickham, L. R. Sita, *Polym. Prepr.* **2011**, *52(1)*, 225–226.

[170] J. Wei, W. Zhang, R. Wickham, L. R. Sita, *Angew. Chem.* **2010**, *122*, 9326–9330; *Angew. Chem. Int. Ed.* **2010**, *49*, 9140–9144.

[171] J. Wei, W. Zhang, L. R. Sita, *Angew. Chem.* **2010**, *122*, 1812–1816; *Angew. Chem. Int. Ed.* **2010**, *49*, 1768–1772.

[172] L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414–6415.

[173] V. M. Möhring, G. Fink, *Angew. Chem.* **1985**, *97*, 982–984; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1001–1003.

[174] Z. Guan, P. M. Cotts, E. F. McCord, S. J. McLain, *Science* **1999**, *283*, 2059–2062.

[175] a) L. K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 267–268; b) S. Mecking, L. K. Johnson, L. Wang, M. Brookhart, *J. Am. Chem. Soc.* **1998**, *120*, 888–899.

[176] D. P. Gates, S. A. Svejda, E. Oñate, C. M. Killian, L. K. Johnson, P. S. White, M. Brookhart, *Macromolecules* **2000**, *33*, 2320–2334.

[177] a) L. Johnson, A. Bennett, K. Dobbs, E. Hauptman, A. Ionkin, S. Ittel, E. McCord, S. McLain, C. Radzewich, Z. Yin, L. Wang, Y. Wang, M. Brookhart, *Polym. Mater. Sci. Eng.* **2002**, *86*, 319; b) L. Wang, E. Hauptman, L. K. Johnson, W. J. Marshall, E. F. McCord, Y. Wang, S. D. Ittel, C. E. Radzewich, K. Kunitsky, A. S. Ionkin, *Polym. Mater. Sci. Eng.* **2002**, *86*, 322; c) L. Johnson, L. Wang, S. McLain, A. Bennett, K. Dobbs, E. Hauptman, A. Ionkin, S. Ittel, K. Kunitsky, W. Marshall, E. McCord, C. Radzewich, A. Rinehart, K. J. Sweetman, Y. Wang, Z. Yin, M. Brookhart, *ACS Symp. Ser.* **2003**, *857*, 131–142.

[178] a) L. S. Moody, P. B. MacKenzie, C. M. Killian, G. G. Lavoie, J. A. Ponasik, Jr., A. G. M. Barrett, T. W. Smith, J. C. Pearson, (Eastman Chemical), WO 00/50470, **2000**; b) L. S. Moody, P. B. MacKenzie, C. M. Killian, G. G. Lavoie, J. A. Ponasik, Jr., T. W. Smith, J. C. Pearson, A. G. M. Barrett, (Eastman Chemical), US 6 946 532, **2005**.

[179] M. Schmid, R. Eberhardt, M. Klinga, M. Leskelä, B. Rieger, *Organometallics* **2001**, *20*, 2321–2330.

[180] M. A. Zuideveld, P. Wehrmann, C. Röhr, S. Mecking, *Angew. Chem.* **2004**, *116*, 887–891; *Angew. Chem. Int. Ed.* **2004**, *43*, 869–873.

[181] D. Meinhard, M. Wegner, G. Kipiani, A. Hearley, P. Reuter, S. Fischer, O. Marti, B. Rieger, *J. Am. Chem. Soc.* **2007**, *129*, 9182–9191.

[182] D. H. Camacho, E. V. Salo, J. W. Ziller, Z. Guan, *Angew. Chem.* **2004**, *116*, 1857–1861; *Angew. Chem. Int. Ed.* **2004**, *43*, 1821–1825.

[183] S. Mecking, *Macromol. Rapid Commun.* **1999**, *20*, 139–143.

[184] L. C. Simon, H. Patel, J. B. P. Soares, R. F. de Souza, *Macromol. Chem. Phys.* **2001**, *202*, 3237–3247.

[185] J. R. Severn, J. C. Chadwick, V. V. A. Castelli, *Macromolecules* **2004**, *37*, 6258–6259.

[186] R. Huang, C. E. Koning, J. C. Chadwick, *Macromolecules* **2007**, *40*, 3021–3029.

[187] H. S. Schrekker, V. Kotov, P. Preishuber-Pflugl, P. White, M. Brookhart, *Macromolecules* **2006**, *39*, 6341–6354.

[188] A. Dorcier, N. Merle, M. Taoufik, F. Bayard, C. Lucas, A. de Mallmann, J. M. Basset, *Organometallics* **2009**, *28*, 2173–2178.

[189] M. M. Wegner, A. K. Ott, B. Rieger, *Macromolecules* **2010**, *43*, 3624–3633.

[190] M. Brookhart, B. L. Small, 9th IUPAC Symposium on Organometallic Chemistry, Göttingen, Germany, July 20–25, **1997**, Poster 447.

[191] B. L. Small, M. Brookhart, A. M. A. Bennett, *J. Am. Chem. Soc.* **1998**, *120*, 4049–4050.

[192] G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White, D. J. Williams, *Chem. Commun.* **1998**, 849–850.

[193] A. M. A. Bennett, (DuPont), WO 98/27124, **1998**.

[194] G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redshaw, G. A. Solan, S. Strömberg, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1999**, *121*, 8728–8740.

[195] S. K. Moore, *Chem. Week* **2000**, Feb. 16, 21.

[196] B. L. Small, M. Brookhart, *J. Am. Chem. Soc.* **1998**, *120*, 7143–7144.

[197] a) S. Mecking, (Targor GmbH), US 6 262 196 B1, **2001**; b) S. Mecking, (Basell Polyolefine GmbH), EP 963 385 B1, **2004**; c) S. Mecking, (Basell Polypropylen GmbH), US 6 384 144 B1, **2002**.

[198] a) S. Mihan, F. Fantinel, (Basell Polyolefine GmbH), US 7 723 448 B2, **2010**; b) S. Mihan, R. Karer, H. Schmitz, D. Lilge, (Basell Polyolefine GmbH), US 8 003 740 B2, **2011**.

[199] A. Kurek, S. Mark, M. Enders, M. O. Kristen, R. Mülhaupt, *Macromol. Rapid Commun.* **2010**, *31*, 1359–1363.

[200] a) G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, G. Moraglio, *J. Am. Chem. Soc.* **1955**, *77*, 1708–1710; b) G. Natta, F. Danusso, D. Sianesi, *Makromol. Chem.* **1958**, *28*, 253–261.

[201] N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules* **1986**, *19*, 2464–2465.

[202] *Syndiotactic Polystyrene* (Ed.: J. Schellenberg), Wiley, Hoboken, **2010**.

[203] N. Ishihara, M. Kuramoto, M. Uoi, *Macromolecules* **1988**, *21*, 3356–3360.

[204] C. Pellecchia, P. Longo, A. Grassi, P. Ammendola, A. Zambelli, *Makromol. Chem. Rapid Commun.* **1987**, *8*, 277–279.

[205] N. Tomotsu, N. Ishihara, T. H. Newman, M. T. Malanga, *J. Mol. Catal. A* **1998**, *128*, 167–190.

[206] W. Kaminsky, S. Lenk, V. Scholz, H. W. Roesky, A. Herzog, *Macromolecules* **1997**, *30*, 7647–7650.

[207] J. Schellenberg, N. Tomotsu, *Prog. Polym. Sci.* **2002**, *27*, 1925–1982.

[208] J. Schellenberg, *Prog. Polym. Sci.* **2009**, *34*, 688–718.

[209] A.-S. Rodrigues, E. Kirillov, J.-F. Carpentier, *Coord. Chem. Rev.* **2008**, *252*, 2115–2136.

[210] T. H. Newman, M. T. Malanga, *J. Macromol. Sci. Pure Appl. Chem.* **1997**, *34*, 1921–1927.

[211] J. C. W. Chien, Z. Salajka, S. Dong, *Macromolecules* **1992**, *25*, 3199–3203.

[212] A. Zambelli, C. Pellecchia, A. Proto, *Macromol. Symp.* **1995**, *89*, 373–382.

[213] A. Grassi, S. Saccheo, A. Zambelli, F. Laschi, *Macromolecules* **1998**, *31*, 5588–5591.

[214] J. Schellenberg, H.-J. Leder, *Adv. Polym. Technol.* **2006**, *25*, 141–151.

[215] M. Malanga, *Adv. Mater.* **2000**, *12*, 1869–1872.

[216] N. Ishihara, *Macromol. Symp.* **1995**, *89*, 553–562.

[217] B. L. Goodall in *Late Transition Metal Polymerization Catalysis* (Eds.: B. Rieger, L. Saunders Baugh, S. Kacker, S. Striegler), Wiley-VCH, Weinheim, **2003**, pp. 101–154.

[218] H. Kajiura, H. Oda, S. Minami, (Mitsui), EP 0 156 464 B1, **1985**.

[219] H. Cherdron, M.-J. Brekner, F. Osan, *Angew. Makromol. Chem.* **1994**, *223*, 121–133.

[220] a) C. Mehler, W. Risse, *Makromol. Chem. Rapid Commun.* **1991**, *12*, 255–259; b) N. Seehof, C. Mehler, S. Breunig, W. Risse, *J. Mol. Catal.* **1992**, *76*, 219–228; c) A. Sen, T.-W. Lai,

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Organometallics **1982**, *1*, 415 – 417; d) A. Sen, T.-W. Lai, R. R. Thomas, *J. Organomet. Chem.* **1988**, *358*, 567 – 588.

[221] a) F. Blank, C. Janiak, *Coord. Chem. Rev.* **2009**, *253*, 827 – 861; b) C. Janiak, P. G. Lassahn, *Macromol. Rapid Commun.* **2001**, *22*, 479 – 493; c) C. Janiak, P. G. Lassahn, *J. Mol. Catal. A* **2001**, *166*, 193 – 209.

[222] G. Wilke, *Angew. Chem.* **1988**, *100*, 189 – 211; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 185 – 206.

[223] R. Taube, U. Schmidt, J.-P. Gehrke, P. Böhme, J. Langlotz, S. Wache, *Makromol. Chem. Macromol. Symp.* **1993**, *66*, 245 – 260.

[224] M. D. Walter, R. A. Moorhouse, P. S. White, M. Brookhart, *J. Polym. Sci. Part A* **2009**, *47*, 2560 – 2573.

[225] A. Bell, L. F. Rhodes, B. L. Goodall, J. C. Fondran, (B. F. Goodrich), US 6 350 832 B1, **2002**.

[226] R. G. Gastinger, B. B. Anderson, K. J. Klabunde, *J. Am. Chem. Soc.* **1980**, *102*, 4959 – 4966.

[227] D. A. Barnes, G. M. Benedikt, B. L. Goodall, S. S. Huang, H. A. Kalamarides, S. Lenhard, L. H. McIntosh, III, K. T. Selvy, R. A. Shick, L. F. Rhodes, *Macromolecules* **2003**, *36*, 2623 – 2632.

[228] A. D. Hennis, J. D. Polley, G. S. Long, A. Sen, D. Yandulov, J. Lipian, G. M. Benedikt, L. F. Rhodes, J. Huffman, *Organometallics* **2001**, *20*, 2802 – 2812.

[229] J. Lipian, R. A. Mimna, J. C. Fondran, D. Yandulov, R. A. Shick, B. L. Goodall, L. F. Rhodes, J. C. Huffman, *Macromolecules* **2002**, *35*, 8969 – 8977.

[230] M. Yamashita, I. Takamiya, K. Jin, K. Nozaki, *Organometallics* **2006**, *25*, 4588 – 4595.

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