Discovery and development of metallocene-based polyolefins with special properties

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ABSTRACT

Besides Ziegler-Natta and Phillips catalysts the development of methylaluminoxane (MAO) as cocatalyst in combination with metallocenes or other transition metal complexes for the polymerization of olefins has widely increased the ability of living polymerization. These catalysts allow the synthesis of isotactic, isoblock, syndiotactic, stereoblock or atactic polymers, as well as polyolefin composite materials with superior properties such as film clarity, tensile strength and lower content of extractables. Metallocene and other single-site catalysts are able to copolymerize ethene with propene with stereospecificity in the polymerization of olefins, cyclic olefins, or polar vinyl monomers such as ethers, alcohols or esters, especially if the polar monomers are protected by aluminum alkyls. Different vinyl ethers such as vinyl-ethyl ether, vinyl-propyl ether, vinyl-hexyl ether, and 2,7-octadienyl methyl ether (MODE) were copolymerized with olefins using triisobutylaluminum as protecting agents. Polar monomers could be incorporated into the polymer chain by up to 10 mol%.

INTRODUCTION

In comparison to Ziegler-Natta systems, metallocene catalysts are soluble in hydrocarbons; show only one active site and the metal structure can be easily changed. These qualities would allow to predict the properties of the resulting polyolefins accurately by selecting the active site and the metalocene structure. Only one site is active, so the resulting polymer properties are predictable through the selection of the metalocene and by altering the electronic properties of the monomers. Therefore, one can achieve living polymerization with high selectivity and high tacticity.
conditions. In addition, their catalytic activity is about 100 times higher than the classical Ziegler-Natta systems. Metalloocene in combination with conventional aluminium cocatalyst is, are ed cap be 6 polymerizing ethene, but only at a very low activity. With th d scw ry ad a  icatin 6 met 6 aln i-inoxane (MAO) it was possible to enhance the activity, surprisingly, by a factor of 10,000. Therefore, MAO 6 ayr a craaal 6 rt in th cataly is with metallo en s [1].

The discovery of MAO has been more or less an accident. In the Institute of Technical and Macromolecular Chemistry at the University of Hamburg we h ev b en iv stig tin n sid reacts , esp cially the hydrogen transfer in homogeneous Ziegler-Natta systems [2]. To lower the reaction rate of the tita- n m sy tem, we h ev b en iv stig tin n th reacts ion b tw een b scv lp n ad ec -5 ti tan m id meth ad trime aln im c e s is b ev j s lw 6-hydrogen transfer (Equation 1).

\[
\text{Cp}_2\text{Ti(CH)}_3 + \text{Al} (\text{CH})_3 \rightarrow \text{Cp}_2\text{Ti-CH}_2\text{Al} (\text{CH})_3 + \text{CH}_3
\]

This slow reaction and the complexation by ethene has been analyzed by NMR measurements, that there is no reduction of titanium (IV) and no polymerization take place. In an incident in 1975 the uninentonal condensation of water into the NMR tube led to the astonishing formation of polyethylene [3]. This unexpected observation confirmed in a larger scale experiment in a 1 L autoclave [4]. More details of this discovery can be found in published reports [5, 6]. The polymerization rate in a halogen of \text{Cp}_2\text{Ti(CH)}_3 / Al(\text{CH})_3 / H_2O-catalyst reached a maximum, when a high amount of water with its maximum ratio of 1:1 with trimethylaluminum was added. It was clear that trimethylaluminum (TMA) reacted rapidly with water in toluene. The next step was therefore to isolate the product, formed in a 1:1 mixture of water and trimethylaluminum in solvents, in order to avoid explosions. The general reaction followed as in Equation 2.

\[
\text{nH}_2\text{O} + (n + 1) \text{Al} (\text{CH})_3 \rightarrow (\text{H}_2\text{C})_2\text{Al}[\text{O-}\text{AlCH}_3]_n - \text{CH}_3 + 2n \text{CH}_4
\]

[Figure 1. Structures of cyclic and linear MAO, big balls: aluminium, small balls: oxygen, and methyl groups]

After 20 hours, the reaction mixture was filtrated and the solvent evaporated. The white powder obtained was dried and analyzed. The compound was named methylaluminoxane. MAO was investigated by element analysis, cryoscopic and NMR measurements, and decomposition with HCl. It was found that MAO was a mixture of different oligomers, including some ring structures (Figure 1).

\[ \text{Cp}_2\text{Ti(CH)}_3 + \text{Al} (\text{CH})_3 \rightarrow \text{Cp}_2\text{Ti-CH}_2\text{Al} (\text{CH})_3 + \text{CH}_3 \]

As the aluminum atoms in the unit structures of MAO are coordinate unsaturated, the units join together forming clusters and cages. These have molecular weights from 1200 to 1600, measured by cryoscop in benzene and are soluble in hydrocarbons especially in aromatic solvents. A probable association and cage like structure of four \text{[Al}_2\text{O}_2\text{Me}_4\text{]} n its are shown in Figure 2.

The nature of the polymerization active site of metalloenc/MAO catalysts and the role of MAO are not fully understood. One function of MAO is the alk atin 6 th metallo en cm 6 ex in case th t a dichloride is used. The other is the formation of an ion-pair. Marks [9] and Bochmann [10], showed that th activ ty 6 metallo en cataly ts d p d n th formation of cationic species. Today, most research groups agree with this statement. The bulky MAO...
Homo-polyolefins

Metalloenes, especially zirconocenes and also titanocenes, hafnocenes, and MAO treated transition metal complexes are highly active for the polymerization of olefins, dieolefins, and styrene and have motivated several research papers and publications in the last 20 years. An overview can be found in selected review articles and a 2015 review. It could be shown that a soluble catalyst, such as Cp₂ZrCl₂/MAO is able to produce polyethylene with high MBIL and weight distribution of approximately two. All active sites are similar and form polymer chains with the same average chain length (single site catalysts). Only traces of low molecular weight oligomers are formed. Zirconocene catalysts with different silanes and ZrH₂Cl₂-Et₂LEW are used as interannular bridges between the rings. Central metals could be 1) Zr, Hf. Such and similar metalloenes are used for the polymerization of ethene, propene, and other olefins.

Table 1. Comparison of ethene polymerization with different metalloene/methylaluminoxane catalysts at same polymerization conditions

<table>
<thead>
<tr>
<th>Metallocene (Met)</th>
<th>Activity [kg PE/(mol x h x 10⁶)]</th>
<th>Molecular weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₂TiCl₂</td>
<td>111900</td>
<td>620000</td>
</tr>
<tr>
<td>Cp₂ZrCl₂</td>
<td>15500</td>
<td>620000</td>
</tr>
<tr>
<td>Cp₂HfCl₂</td>
<td>16600</td>
<td>620000</td>
</tr>
<tr>
<td>Cp₂ZrCl₂</td>
<td>78000</td>
<td>320000</td>
</tr>
<tr>
<td>[Ph₂Si(Ind)₂]ZrCl₂</td>
<td>22200</td>
<td>480000</td>
</tr>
<tr>
<td>[Cp₂TiCl₂]</td>
<td>12000</td>
<td>350000</td>
</tr>
<tr>
<td>[Cp₂HfCl₂]</td>
<td>2900</td>
<td>480000</td>
</tr>
<tr>
<td>[Cp₂ZrCl₂]</td>
<td>78000</td>
<td>190000</td>
</tr>
<tr>
<td>[Me₂Si(2Me-4Ph-Ind)₂]ZrCl₂</td>
<td>119190</td>
<td>250000</td>
</tr>
<tr>
<td>[Me₂Si(2Me-4Ph-Ind)₂]ZrCl₂</td>
<td>16600</td>
<td>730000</td>
</tr>
<tr>
<td>[Me₂Si(Ind)₂]ZrCl₂</td>
<td>13900</td>
<td>320000</td>
</tr>
<tr>
<td>[Ph₂Si(Ind)₂]ZrCl₂</td>
<td>20200</td>
<td>620000</td>
</tr>
<tr>
<td>[Ph₂Si(Ind)₂]ZrCl₂</td>
<td>3300</td>
<td>180000</td>
</tr>
<tr>
<td>[Me₂Si(Ind)₂]ZrCl₂</td>
<td>2000</td>
<td>500000</td>
</tr>
<tr>
<td>[Me₂Si(Ind)₂]ZrCl₂</td>
<td>2800</td>
<td>630000</td>
</tr>
<tr>
<td>[Me₂Si(Ind)₂]ZrCl₂</td>
<td>890</td>
<td>560000</td>
</tr>
</tbody>
</table>

(a) Ethene pressure = 2.5 bar, temperature = 30°C, [metalloene] = 6.25x10⁻⁵ mol, metalloene/MAO = 250, solvent = toluene. (b) Cp = cyclopentadienyl, Me = methyl, Ind = indenyl, IndH₂ = tetrahydroindenyl, En = C₅H₅, Flu = fluorenyl, NmCp = neomenthyl cyclopentadienyl, Bz = benzyl
**Polyethylenes**

Table 1 compares the polymerization of ethene by selected metalloocene/methylaluminoxane catalysts [23, 24].

Generally zirconium catalysts are more active than hafnium or titanium systems. Especially, trimethyl substituted bisindenyl systems show very high activities, except for sterically less hindered Cp₂ZrCl₂. When pentamethyl cyclopenta - dienyl - zirconium dichloride (Cp’₂ZrCl₂/MAO) is used instead of Cp₂ZrCl₂/MAO, a polyethylene of much higher molecular weight, though a lower activity is formed. This means that chain transfer reactions are much slower in the substituted zirconocene complex. The molecular weight of the polymer is lower by increasing the temperature, raising the polymer weight of metalloocene polyethylene in the wide range between 18 000 and 1.5 million and can be easily lowered by raising the temperature ratio.
metallicen/ethene ratio, or by adding small amounts of hydrogen (0.1–2 mol%). Other zirconium complexes have linked amidofoxylenyl ligands [25]. The molecules are usually distributed in capital letters, e.g., Nm: neomenthyl; Ind: indenyl; Fluo: fluorenyl; En: C₆F₄; BenzInd: benzindenyl; Cp: cyclopentadienyl; HfCl₂: hafnium chloride; ZrCl₂: zirconium chloride; Cp₂ZrCl₂: bis(cyclopentadienyl)zirconium dichloride; Cp₅ZrCl₃: pentacarbonylzirconium trichloride.

For an industrial use it is necessary to support the MAO cocatalyst on silica or alumina. Silica with a high quantity of MAO, up to 30 wt%, can be obtained. In such a case a heterogeneous Ziegler-Natta catalysts (drop-in technology) [28]. By this procedure a better process as for heterogeneous Ziegler-Natta catalysts (drop-in technology) [28].

**Polypropylenes**

By metallocene/MMAO catalysts it is possible to produce microtactic propylene using atactic, isotactic, and syndiotactic polypropylene in combination with MAO in toluene solution [30].

In 1987 Ewen, Jones, and Razavi [31] obtained pure s syndiotactic, p isotactic, and m atactic isomers of propylene using a Cs,symmetric metallocene complex with hydrogen atoms of the backbone chain not shown)

Table 2. Comparison of propene polymerization (a) with different metallocone/methylaluminoxane catalysts at same polymerization conditions

<table>
<thead>
<tr>
<th>Metallocone</th>
<th>Activity</th>
<th>Molecular weight (g/mol)</th>
<th>Isotacticity (mmmm)</th>
<th>Microstructure (d)</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₂ZrCl₂</td>
<td>140</td>
<td>2 000</td>
<td>7</td>
<td>a</td>
<td>118</td>
</tr>
<tr>
<td>(NmCp₂)ZrCl₂</td>
<td>170</td>
<td>3 000</td>
<td>23</td>
<td>sb</td>
<td>136</td>
</tr>
<tr>
<td>(EnInd)ZrCl₂</td>
<td>1 690</td>
<td>32 000</td>
<td>91</td>
<td>i</td>
<td>126</td>
</tr>
<tr>
<td>(EnInd)HCl₂</td>
<td>610</td>
<td>40 000</td>
<td>85</td>
<td>ib</td>
<td>126</td>
</tr>
<tr>
<td>(En(2,7Me₂Ind)₂)ZrCl₂</td>
<td>750</td>
<td>418 000</td>
<td>&gt;99</td>
<td>i</td>
<td>162</td>
</tr>
<tr>
<td>(Me₅Si(2Me₂Ind)₂)ZrCl₂</td>
<td>1 940</td>
<td>79 000</td>
<td>96</td>
<td>i</td>
<td>148</td>
</tr>
<tr>
<td>(Me₅Si(2,7Me₂Ind)₂)ZrCl₂</td>
<td>2 160</td>
<td>90 000</td>
<td>96</td>
<td>i</td>
<td>136</td>
</tr>
<tr>
<td>(Me₅Si(2Me₂-4PhInd)₂)ZrCl₂</td>
<td>15 000</td>
<td>650 000</td>
<td>95</td>
<td>i</td>
<td>155</td>
</tr>
<tr>
<td>(Me₅Si(2Me₂-4,5-BenzInd)₂)ZrCl₂</td>
<td>6 100</td>
<td>380 000</td>
<td>95</td>
<td>i</td>
<td>160</td>
</tr>
<tr>
<td>(Ph₅C(2,3Fluo(Cp)₂)ZrCl₂</td>
<td>1 980</td>
<td>729 000</td>
<td>98</td>
<td>i</td>
<td>157</td>
</tr>
<tr>
<td>(Me₅C(2,3Fluo(Cp)₂)ZrCl₂</td>
<td>1 550</td>
<td>159 000</td>
<td>98</td>
<td>s</td>
<td>141</td>
</tr>
<tr>
<td>(Me₅C(2,3Fluo(Cp)₂)HCl₂</td>
<td>130</td>
<td>750 000</td>
<td>98</td>
<td>s</td>
<td>138</td>
</tr>
<tr>
<td>(Me₅C(2,3Fluo(3-tBuCp)₂)ZrCl₂</td>
<td>1 045</td>
<td>52 000</td>
<td>89</td>
<td>ib</td>
<td>130</td>
</tr>
</tbody>
</table>

(a) Propene pressure = 2 bar; temperature = 30°C; metallocone = 6.25×10⁻⁶ mol, metallocone/MAO = 250; solvent = 200 mL toluene; (b) Cp = cyclopentadienyl; Nm = neomenthyl; Ind = indenyl; En = C₆F₄H₂; BenzInd = benzindenyl; Fluo = fluorenyl; (c) in kg PP/(mol Zr/Hf.h.); (d) a = atactic; i = isotactic; s = syndiotactic; sb = stereoblock; ib = isoblock

Figure 4. Microstructures of polypropylenes obtained by various metallocone catalysts (hydrogen atoms of the backbone chain are not shown)
component. Non-chiral *ansa*-metallo en s su h as [(CH₃)₂Si(Flu)]₂ZrCl₂ (Figure 3) produce atactic polypropylene.

**Polyolefin nanocomposites**

Polyolefin nanocomposites are of great interest because such materials with new properties [34]. The properties of the nanocomposites are not only influenced by the kind of fillers but also by the morphology of the polyolefins and the preparation process. Metalloocene catalysts are soluble in ar a d b d a h e n the surface of the nanofillers such as particles, fibers, layered silica, carbon nanofiber (CNF), multi-walled carbon nanotubes (MWCNT), changing the surface to a hydrophobic one [35, 36]. The MAO reacts, for example, with the OH-groups of silica or with carboxy groups of oxidized carbon nanotubes and are physically absorbed at the surface (Figure 3). Methane is formed by the chemical reaction of MAO with polar groups.

Excess MAO is washed out, in a second step, the metallo en s ad e a m ng catalytically active polymerization sites on the nanosurface. The thickness of the polymer films, formed by addition of ethene or propene, depends on the polymerization conditions, especially the polymerization time, the kind of metalloene catalyst, and the pressure of the monomer. The in-situ polymerization leads to composite materials where the particles or fibers are intensively covered with the polymer.

The composite materials show, for example, an imp u d sti s ss with a u b i e l o s i m p et strength, high gas barrier properties, significant flame retard n , b tter clarity, ad glo s as well as h cry -
tallization rates. Even low nanoparticle contents are already sufficient to obtain new or modified material characteristics, especially a faster crystallization rate and a higher crystallization temperature.

Carbon nanofibers (CNF) or multiwalled carbon nanotubes (MWCNT) are an especially attractive class of fillers for polymers because of their intriguing mechanical and thermal properties [37].

Multi-walled carbon nanotubes (MWCNT) were sonicated in a toluene suspension, treated by MAO stirred for 24 hours, filtrated, and washed with hot toluene [38]. After adding the chiral *ansa*-zirconocene [(CH₃)₂Si(2-CH₃-4-Nap-Ind)]ZrCl₂, ad p 𝑛 p 𝑛, isotactic high molecular weight polypropylene iPP/MWCNT composites with 0.9 – 50 wt% filler content were obtained. The molecular weights of the polypropylene matrix in the nanocomposites were in the range of Mₘ = 1,200,000 – 1,700,000. The polymerization activity reached 5000 kg PP/mol Zrₙₙₚₚₚₚₚ [propene]. It was independent of the filler content. As expected for in-situ polymerization, the polymer grew directly on the fiber surface and covered them with a thin PP layer. The dihed p 𝑛 p e n a m 𝑝 ites were b tine d in powder form. By longer polymerization times, the thickness of the polyolefin covering the fiber increased. The fiber/MAO/zirconocene system worked like a supported catalyst. Filler contents between 0.5 up to 50 wt% were possible.

The morphology of the isotactic PP/CNF nanocomposites was investigated by transmission electron microscopy (TEM). It can be seen from Figure 6 that the nanotubes are coated by a thin film of iPP. The diameter of the MWCNT used (about 20 layers) is 20 nm and the thickness of the iPP coat is about 8 nm.

![Figure 5. Formation of polymerization active sites by absorption of MAO on oxidized multiwall carbon nanotubes (MWCNT) followed by adding a zirconocene](image1)

![Figure 6. TEM micrographs of a MWCNT composite prepared by in-situ polymerization covered by iPP (left), top of a nanotube/iPP composite by higher resolution (right)](image2)
ated PP b s t y se v rated fr e ach b b r is p r e f ee th p y er a d s e e m s to b w d n g by the growth of the polymer chains.

The main advantage of CNF or MWCNT filled PP is the change of mechanical properties. High molecular weight isotactic polypropylene filled with MWCNT is an exceptionally strong composite material. The tensile strength of a composite film increases by 20% if only 1 wt% of MWCNT is incorporated but also the form stability and the crystallization rate from a melt in resi ng y ma th s ce ma l mate r su tab e w ap icat e su h as in th at mo tive plas tic ind u s t ies [39].

**Copolymers**

Metalloocene/MAO catalysts are not only suitable for the homopolymerization of ethene and propene but also for copolymerization with different comonomers [25, 40, 41]. Copolymers with new microstructures and properties are:

- Ethene – propene (EP)
- Ethene – propene, diene (EPDM)
- Ethene – 1-butene, hexene (LLDPE)
- Ethene – 1-octene (LLDPE)
- Ethene – 1,5-hexadiene (elastomer)
- Ethene – cyclopentene (COC)
- Ethene – norbornene (elastomer)
- Ethene – 1,3-butadiene (elastomer)
- Ethene – styrene (elastomer)

EP, EPDM (ethene propene diene monomers), LLDPE (linear low density polyethylene) are of high interest for polymer industries. All copolymers produced by metalloocene catalysts are characterized by a narrow molecular weight distribution of 2 and a uniform microstructure. While the comonomers are distributed randomly in the p y er ch in h y la am o s are a e d d to d cres th d n it a d th mel t of ethene copolymers. The low amount of oligomers compared to copolymers produced by Ziegler-Natta catalysis is resp e f e a h y re a n h oth me chan ical prop erties of the obtained LLDPE. Mechanical properties can be increased if there are some long chain branches in the polymer chain. Long-chain branched polyethylenes can be obtained by copolymerization of ethene with ethene oligomers by tandem polymerization in one step [42] or with ethene/propene oligomers in two steps [43]. In the last case the re are b ai d p y ers with cy r tallin polyethylene backbone chains and amorphous ethene/propene copolymer side chains.

Figure 7 shows a scheme for the preparation of a ch in b a h d p y th ce b y usi ng two dif fer ent metalloocene catalysts in two steps. In a first step ethene/propene macromers were produced by a [(C₃H₆)₅]₂ZrCl₂/MAO catalyst with molecular weights of 8 000 to 25 000 g·mol⁻¹ (Step A). The propene content varied from 13 to 23 wt%. The macromers were amorphous, show a high content of vinyl end-groups. In the following copolymerization of the ethene/propene macromers with ethene and different metalloocene [Ph₂C(2,7-di-tert-Bu,Flu)(Cp)]₂ZrCl₂ was used to catalyze the copolymerization (Step B). Small amounts of ethylene were added to reduce the mb ceth ar weih for easier rheological measurements.

By the copolymerization of cyclic olefins such as cycloolefin copolymers (COC) rep es f a w class b th r mp a stic, am o p as [44, 45]. Cyclopentene, norbornene or other cyclic olefins are incorporated exclusively by 1,2-insertion into the g w cg p y er ch in n rig opening occurs. The insertion of the huge norbornene monomer is very fast by metalloocene/MAO catalysts. The CP₅C(Ind)(Cp)₂ZrCl₂/MAO catalyst shows not only high activities for the copolymerization of ethene

**Table 3. Copolymerization** (a) of norbornene (N) and ethene by different metalloocene/MAO-catalysts

<table>
<thead>
<tr>
<th>Metallocene²⁺</th>
<th>t (min)</th>
<th>Activity (kg/mol h)</th>
<th>Incorp of norbornene (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₅ZrCl₂</td>
<td>30</td>
<td>1200</td>
<td>21.4</td>
</tr>
<tr>
<td>[En(Ind)₂]ZrCl₂</td>
<td>10</td>
<td>9120</td>
<td>26.1</td>
</tr>
<tr>
<td>[Me₅Si(Ind)₂]ZrCl₂</td>
<td>15</td>
<td>2320</td>
<td>28.4</td>
</tr>
<tr>
<td>[En(IndH₂)₂]ZrCl₂</td>
<td>40</td>
<td>480</td>
<td>28.1</td>
</tr>
<tr>
<td>[Me₅C(Flu)(Cp)]ZrCl₂</td>
<td>10</td>
<td>7200</td>
<td>28.9</td>
</tr>
<tr>
<td>[Ph₅C(Flu)(Cp)]ZrCl₂</td>
<td>10</td>
<td>6000</td>
<td>27.3</td>
</tr>
<tr>
<td>[Ph₅C(Ind)(Cp)]ZrCl₂</td>
<td>15</td>
<td>2950</td>
<td>33.3</td>
</tr>
</tbody>
</table>

Ethene pressure = 2 bar, [N] = 0.05 mol/L, temperature = 30°C, [metallocene] = 5×10⁻⁵ mol/L, metalloocene/MAO = 200, Solvent = toluene; (b) Cp = cyclopentadienyl, Me = methyl, Ind = indenyl, En = C₅H₅, Flu = fluorenyl, Ph = phenyl.
with a boronate, but gives an alternating structure, as well as some other copolymers with a statistical structure, few others produce polymers with an alternating structure. Statistical copolymers are amorphous if the molecular weight is more than 10-15 mol% of cycloolefins are incorporated in the polymer chain. The glass transition temperature can be varied over a wide range by the composition of norbornene as cycloolefin and variation in its amount in the polymer chain. Cycloolefin copolymers are characterized by excellent transparency, high glass transition temperatures of up to 200°C and excellent long-life service temperatures. They are resistant to polar solvents and chemicals and can be melt-processed. Due to their high carbon/hydrogen ratio, these polymers have a high refractive index (1.53 for an ethene/norbornene copolymer at 50 mol% incorporation). Their stability against thermal degradation is adequate, and they are used in 50% incorporation. Their stability against thermal degradation is adequate, and they are used in various fields such as solar cells, lenses, optical fibers, and films.

**Polyolefins with polar comonomers**

The introduction of polar groups into polyolefins to improve their characteristics can be achieved through the use of metal-based catalysts. With the introduction of polar groups, the properties of the copolymers can be modified to meet the requirements of various applications. For example, in the field of optical fibers, the introduction of polar groups can improve the optical properties and reduce the attenuation. The functionalization of polyolefins offers a possibility to broad applications in areas, less explored before. Only few functionalization processes are available.

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**Figure 7.** Reaction scheme for ethene-graft ethene/propene copolymers by two different zirconocene/MAO catalysts in two steps.
ture. Metallocene and other single site catalysts are able to polymerize ethene and polar vinyl monomers, such as ethyl, propyl, butyl, and hexyl esters with high activities after posttreatment with Ti monocarbonyl. Among all functional groups, oxygen-substituted olefins are the most studied for copolymerization with ethene and propene. These groups are of interest, because of their possibility to be a precursor for potential polyolefin elastomers, since the introduction of these functionalities may lead to the formation of materials with high chemical reactivity.

For the copolymerization of ethene with polar monomers in this work are used:

- Allyl ethyl ether (AEE)
- Allyl propyl ether (APE)
- 5-Hexenyl butyl ether (HBE)
- 9-Decenyl butyl ether (DBE)
- 2,7-Octadienyl methyl ether (MODE)

These ethers are available by organic synthesis or through the reaction of ethene with alcohols in the presence of a Lewis acid catalyst. The structure of the vinyl ethers used is shown in Figure 8.

**EXPERIMENTAL**

The polymerization experiments were performed using standard Schlenk, syringe, and glovebox techniques. Argon was purchased from Linde and purified by passing through an Oxisorb cartridge. Ethene (Linde) and toluene were purified by passing through columns with BASF R3-11 catalyst and a 3 Å molecular sieve. A solution in toluene (1 mol/L) of the different vinyl ethers was dried over molecular sieves for 48 h and then stirred for 3 h with triisobutylaluminium (TIBA) followed by a distillation under vacuum at 100°C.

All polymerization runs were performed in a Büchi BEP 280 laboratory autoclave with a Type I glass pressure vessel. Temperature was adjusted with a heat jacket connected to a thermostat allowing adjustment of the polymerization temperature with an accuracy of ±0.5°C. During the polymerization runs, the ethene pressure was kept constant. The ethene consumption was monitored with a Brooks 5850 TR mass flow meter. For a typical polymerization experiment, the reactor was evacuated at 95°C for 1 h and then cooled down to the desired temperature. Subsequently, the reactor was charged with 400 mg MAO, comonomer solution and toluene up to a volume of 200 mL, followed by ethene to the desired feed composition. The polymerization was started by injection of the catalyst solution with a metallocene concentration of 1-5×10⁻⁴ mol/L. The reaction was quenched by addition of 5 mL HCl/ethanol. The obtained polymer was stirred overnight with dilute hydrochloric acid. After phase separation, the polymer was precipitated using ethanol, filtered, washed with ethanol, and dried under vacuum at 40°C until the polymer weight became constant.

The obtained copolymers were characterized by ¹³C-NMR recorded on a Bruker Avance 400 Ultrashield spectrometer. Polymer samples were measured at 100.62 MHz and 100°C using 200 mg of polymer in 2.3 mL of 1,2,4-trichlorobenzene (TCB) and 0.5 mL of 1,1,2,2-tetrachloroethane-d₂. Chemical shifts are reported relative to the CDC₁₃ standard (d 74.24 ppm).

For ¹H-NMR, the samples were prepared by dissolv-
ing the polymer (10-20 mg) in a mixture of 1,2,4-trichlorobenzene (TCB) and of 1,1,2,2-tetrachloroethane-d2 (TCE-d2) and measured at 120°C. All chemical shifts were referred to the solvent of TCE-d2 at 5.94 ppm.

Differential scanning calorimetry measurements were performed on a Mettler Toledo DSC 821 instrument under a nitrogen atmosphere. All samples were prepared in hermetically sealed pans (5-8 mg/sample), and were measured using an empty pan as reference. Calibratation was made using a standard ad for the platinum metal. The melting temperature (T_m) was taken from the second thermal cycle exclusively.

High-temperature gel permeation chromatography (GPC) measurements were performed in 1,2,4-trichlorobenzene at 140°C using a Waters GPC 2000 instrument with HT 106, 104, and 103 Å columns. The Mn was determined by a cm u d with a refractive index x ad the flame photometer, and from a step function, the molecular weight (M_w) of each polymer. Calibration was applied using polystyrene standards (PSS).

The samples were placed in an elemental analyzer connected to a mass spectrometer. Subsequently, they were combusted at 1040°C and the gas was pushed through an oxidation core. The gas resulting after combustion was analyzed by an IRMS mass spectrometer. The ions were separated and detected by a field ion mass spectrometer.

### RESULTS AND DISCUSSIONS

For the polymerization of ethene and allyl ethyl ether the zirconocene [(CH_3)_2Si(Ind)_2]ZrCl_2 and MAO were used. Table 4 shows the polymerization results.

Table 4 shows that it is possible to copolymerize allyl ethyl ethers with 
co en ratio d creases with an increasing co en ratio too. Allyl ethyl ether was incorporated with the highest value of 3.2 mol% which are about 9 wt%. The incorporation increased when the pressure of ethene was dropped to 1 bar. A copolymer with 16 mol% of AEE was obtained by using [(CH_3)_2Si(2-CH_2-4-Naph-Ind)_2]ZrCl_2 as zirconocene. As expected, the melting points of the copolymers decreased strongly from 140°C for pure polyethylene to 108°C for a copolymer with 3.2 mol% of AEE. By the same polymerization conditions, it is more difficult to incorporate the longer chain allyl ethers HBE and DBE. Very high activities of 54,000 or 79,000 kg copolymer/g Zr.h were obtained by the copolymerization of HBE or DBE (0.01 mol/L) in the feed with ethene. This value decreased to only 540 kg copolymer/g Zr.h by a concentration of 0.05 mol/L of DBE. The decrease was not so strong for HBE.

The solubility of the obtained copolymers was poor and made a structure characterization difficult. A typical H-NMR- spectrum is shown in Figure 9.

A significant observation is the complete absence of a signal referent to th v g p of th ar mol -

<table>
<thead>
<tr>
<th>Comonomer</th>
<th>Concentration (mol/L)</th>
<th>Activity</th>
<th>Molecular weight (g/mol)</th>
<th>Incorporation (mol%)</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEE</td>
<td>0.02</td>
<td>5 000</td>
<td>530 000</td>
<td>1.1</td>
<td>123</td>
</tr>
<tr>
<td>AEE</td>
<td>0.04</td>
<td>3 500</td>
<td>450 000</td>
<td>2.0</td>
<td>110</td>
</tr>
<tr>
<td>AEE</td>
<td>0.05</td>
<td>1 600</td>
<td>420 000</td>
<td>3.2</td>
<td>108</td>
</tr>
<tr>
<td>HBE</td>
<td>0.01</td>
<td>54 600</td>
<td>194 000</td>
<td>0.14</td>
<td>139</td>
</tr>
<tr>
<td>HBE</td>
<td>0.025</td>
<td>1 400</td>
<td>105 000</td>
<td>0.60</td>
<td>132</td>
</tr>
<tr>
<td>DBE</td>
<td>0.01</td>
<td>79 300</td>
<td>117 000</td>
<td>0.1</td>
<td>137</td>
</tr>
<tr>
<td>DBE</td>
<td>0.02</td>
<td>3 760</td>
<td>125 000</td>
<td>0.3</td>
<td>131</td>
</tr>
<tr>
<td>DBE</td>
<td>0.03</td>
<td>2 440</td>
<td>130 000</td>
<td>0.3</td>
<td>132</td>
</tr>
<tr>
<td>DBE</td>
<td>0.05</td>
<td>540</td>
<td>346 000</td>
<td>0.6</td>
<td>126</td>
</tr>
</tbody>
</table>
Figure 9. $^1$H-NMR spectra of allyl ethyl ether (AEE) monomer (top) and AEE/ethene copolymer (down A,B,C)

In order to investigate the rule of an ether with a methyl group after the oxygen atom, a definite amount of MAO was used. The polymerization rate was the highest at all temperatures. Only a small amount of MAO was required for the polymerization activity, which was varied between 200 and 400 mg. With an increase in the MAO concentration, the catalytic activity rapidly reached a maximum twofold of its initial activity. This result was also observed for the copolymerization of ethylene and HBE and DBE.

In the copolymerization rates, melting point and molecular weight of the monomer were present in the ether structure. The reaction. The molecular weights varied between 530,000 and 125,000. With an increase in the monomer the molecular weight decreased. The same trend was observed with an increase in the concentration of the vinyl ether. In general, at 45°C the incorporation of AEE shows a maximum.

In a comparison a more bulky zirconocene such as (rac-[Me,Si(2-Me-4-(1-Naph)Ind)]ZrCl$_2$) was used. Surprisingly, the activities for the copolymerization with APE were higher than those for AEE. At an ether concentration of 0.05 mol/L in the feed for APP were obtained 12,000 kg copolymer/g Zr h, while this was only 6,500 for APP. The decrease of the activity with the ether concentration in the feed was higher for APE than for AEE. This result suggested that the presence of one more methyl group in the structure of APE could reduce the negative influence on the ether group on the catalytic activity. If, however, more methyl groups were present in the structure of AEE, the activities dropped again compared to AEE (see Table 4).

Figure 10 shows the dependence of the incorporation rate of ethylene with an atomic ratio of 0.04 mol/L. The molecular weights of APE/ethene copolymer decreased with an increase in the incorporation rate of APE and are 132°C by 2 mol%, 110 by 4.5
A decrease in the catalytic activity was observed both in the temperatures studied. It was observed that the catalyst activity increased with the presence of the modifier. The physical properties of the copolymers were summarized in Table 6.

The physical properties of the copolymers seem to be temperature dependent. At 45°C, it is clearly observed a decrease trend in the melting point with increase in the monomer concentration. The results of the reaction at 60°C, the catalyst activity remained almost the same as at 45°C with slightly lower Tm in repeat in polar monomer feed. The polydispersity index was about 3 with an increase in the concentration of the feed polar group.

Additionally, it was observed that there was no significant change in the melting point of the obtained polymer with the polymerization temperature. However, the activity of the catalyst was reduced with increase in the monomer concentration.

Table 6. Characterization of MODE/ethene copolymer of different polymerization runs (see Table 5)

<table>
<thead>
<tr>
<th>Run</th>
<th>CMODE (mol/L)</th>
<th>Tm (°C)</th>
<th>δH (J/g)</th>
<th>Mw (Kg/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.04</td>
<td>133</td>
<td>121</td>
<td>182</td>
</tr>
<tr>
<td>7</td>
<td>0.06</td>
<td>136</td>
<td>123</td>
<td>161</td>
</tr>
<tr>
<td>8</td>
<td>0.05</td>
<td>117</td>
<td>122</td>
<td>157</td>
</tr>
<tr>
<td>9</td>
<td>0.13</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>1</td>
<td>0.12</td>
<td>141</td>
<td>152</td>
<td>108</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>134</td>
<td>148</td>
<td>102</td>
</tr>
<tr>
<td>5</td>
<td>0.10</td>
<td>132</td>
<td>148</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>0.04</td>
<td>131</td>
<td>126</td>
<td>113</td>
</tr>
<tr>
<td>6</td>
<td>0.15</td>
<td>128</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

Polymerization conditions: ethene pressure 4bar, toluene volume 200mL, polymerization time 1h, cocatalyst MAO; MODE/TIBA = 1:1, precontacted for 30 min.
Metallocene/MAO and other single site catalysts allow the synthesis of tailored polyolefin structures in a way that was impossible in the years before. The incorporation of metalocene into catalyst structures allows the modeling of reaction kinetics and the polymerization process [50]. Reactor models could be developed using mass characteristics of ethene with moieties such as carbon nanotubes, carbon fibers, or metalloocene. The incorporated functional group contents were determined by elemental analysis. The concentration for mode in the copolymer was 1.4wt% (run 1), 4.3wt% (run 2), 6 wt% (run 3), and 7.1 wt% (run 4, in Table 6). This high incorporation rate of a bulky polar monomer with a midletead was considered a key for further investigations with such a copolymer.

CONCLUSION

The development of metallocene/metalloaluminoxane catalysts allows the realization of new bulky and weakly coordinating cocatalysts such as perfluorophenyl-borate anions and boranes. The development is not complete for new materials with property changes. A soft polyolefin matrix can be combined with hard inorganic particles to develop materials with extreme high tensile strength, such as carbon fibers, carbon nanotubes or polymer fibers. An easy way for the preparation of such polyolefin nanocomposites is the in-situ polymerization using nanoparticles or fibers activated by metallocene/MAO or other single site catalysts. Materials with high resistance to hot metal and electric current, adhesion to metal stability can be obtained as well as a good dispersion of the nanofillers in the polymer matrix.

A lot can be done to tailor the microstructure of co-
polymers. To design three dimensional crystallizing polyolefins for materials with special properties such as catalyse to memembranes, elastomers, eric adhesion properties, the controlled self-organization by polar groups could be one way. Important for this and for polymer blends of polyolefins with other polymers such mid other polyethylene, polypropylene, ether, ester, siloxy, or amino groups. In these ways, different vinyl ethers such as allyl ethyl octadienylmethyl ether with ethene. The incorporation of these in other ethenes or china in different vinyl ethers. The polymerization temperature, the comonomer concentration and the used metalloocene complex. Blends of small amount of those in titanium metalloocene b sed cop y ers are ad stiffer compatibilized polymers.

The development and commercialization of metallocone/MAO and other single site catalysts have just started and have expanded the polyolefins range of products. New designed catalysts will enlarge the polyolefin industries and the applications of polymers.

REFERENCES


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