Discovery and development of metallocene-based polyolefins with special properties

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ABSTRACT

Beside 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 possibilities in controlling the polymer composition, structure, tacticity and special properties with high precision. These catalysts allow the synthesis of isotactic, atactic, 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 ethylene and propene with ethylene, propylene, or cycloolefins, 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 tris(isobutyl)aluminum as protecting agents. Polar monomers could be incorporated into the polymer chain by up to 15 mol%. Such copolymers show better gas barrier and surface properties, as well as solvent resistance and they are suitable for blends of polyolefins with polyethers and other polyolefin, because of an excellent adhesion of the two polymers. Polyolefins J (2015) 2: 1-16

Keywords: methylaluminoxane; metallocene catalysts; olefin copolymerization; polar monomers; vinyl ethers

INTRODUCTION

In comparison to Ziegler-Natta systems, metallocene catalysts are soluble in hydrocarbons; show only one active site and are micastr in catalytic reactions. These qualities would allow to predict the properties of the resulting polyolefins accurately by selecting the type of active site and its chemical structure. The choice of polar comonomers has a significant impact on the properties of the result polyolefins. Polyolefins with polar comonomers are suitable for applications in which they can be used as a co-polymer with ethylene and propylene.
conditions. In addition, their catalytic activity is about 100 times higher than the classical Ziegler-Natta systems. Metalloenes in combination with conventional \( \text{Al} \text{Me} \text{C} \text{C} \text{C} \) cocatalysts ts, are ed cao b e o polymerizing ethene, but only at a very low activity. With th id sce ry ad a p icatin o methe aln i-noxane (MAO) it was possible to enhance the activity, surprisingly, by a factor of 10,000. Therefore, MAO h a a cell prf rt in th cataly is with metallo en s

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 e b en in stig n sid reactio , esp cially the hydrogen transfer in homogeneous Ziegler-Natta systems [2]. To lower the reduction rate of the titai n m sy tem, we b e b en in stig n sid reactio in b tween b sce r n ad ch -titan m id methe ad trimet ni aln im , is tead b a titan n -id eth ad triet la in m en a iinig sy tem maih y h NMR analysis at low temperatures. The formation of new CH\(_2\)-id titan n aln im en be s is b evi s lw α-hydrogen transfer (Equation 1).

\[
\text{Cp}_2\text{Ti(}\text{CH}_3\text{)}_2 + \text{Al(}\text{CH}_3\text{)}_3 \rightarrow \text{Cp}_2\text{Ti(}\text{CH}_3\text{)}\text{Ti-CH}_2\text{Al(}\text{CH}_3\text{)}_2 + \text{CH}_4
\]

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 unintentional 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 hagogen \( \text{Cp}_2\text{Ti(}\text{CH}_3\text{)}_2 /\text{Al(}\text{CH}_3\text{)}_3 /\text{H}_2\text{O-catalyst} \) 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 trimeth-ylaluminum in solvents, in order to avoid explosions. The general reaction followed as in Equation 2.

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

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 elementary 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).

\[
\begin{array}{c}
\text{E n t y c h en e}\n\end{array}
\]

As the aluminum atoms in the unit structures of MAO are coordinately 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 \([\text{Al},\text{O},\text{Me}_3])_n\) its are shown in Figure 2.

The nature of the polymerization active site of metallocene/MAO catalysts and the role of MAO are not fully understood. One function of MAO is the atm ato o metallo en cm 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 metallo en cataly ts d p a n th formation of cationic species. Today, most research groups agree with this statement. The bulky MAO
Polyolefins, especially zirconocenes and also titanocenes, hafnocenes, and MAO treated transition metal complexes are highly active for the polymerization of olefins, diolefins, and styrene and have motivated intensive research to the synthesis and publications in the last 20 years. An overview can be found in selected review articles and books [14-20]. It could be shown that a soluble catalyst, such as $\text{Cp}_2\text{ZrCl}_2$/MAO is able to produce polyethylene with high molecular weight distribution of approximately two. All active sites are similar to those in the case of low molecular weight oligomers are formed. Zirconocenes with different structures are used in the polymerization. The cyclopentadienyl-, indenyl-, fluorenyl- ligands could be hydrated or substituted by alkyl, aryl, methoxy, siloxy or other groups. Ethynediyl (C$_2$H$_4$), dimethylsilandiyl ((CH$_3$)$_2$Si), or isopropanediyl ((CH$_3$)$_2$C) are mainly used as interannular bridges between the rings [21]. Central metals could be Ti, Zr, Hf. Such and similar metalloene catalysts are used for the polymerization of ethene, propene, and other olefins [22].

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

<table>
<thead>
<tr>
<th>Metalocene ($^{11}$)</th>
<th>Activity [kg PE/ (mol met/ h mol C$_2$H$_4$)]</th>
<th>Molecular weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cp}_2\text{TiCl}_2$</td>
<td>34200</td>
<td>400000</td>
</tr>
<tr>
<td>$\text{Cp}_2\text{ZrCl}_2$</td>
<td>60900</td>
<td>620000</td>
</tr>
<tr>
<td>$\text{Cp}_2\text{ZrCl}_2$</td>
<td>4200</td>
<td>70000</td>
</tr>
<tr>
<td>$\text{Cp}_2\text{HfCl}_2$</td>
<td>1300</td>
<td>1500000</td>
</tr>
<tr>
<td>$\text{En}(\text{Ind})_2\text{HfCl}_2$</td>
<td>22200</td>
<td>1000000</td>
</tr>
<tr>
<td>$\text{En}(\text{Ind})_2\text{ZrCl}_2$</td>
<td>12000</td>
<td>350000</td>
</tr>
<tr>
<td>$\text{En}(\text{Ind})_2\text{ZrCl}_2$</td>
<td>2900</td>
<td>480000</td>
</tr>
<tr>
<td>$\text{En}(2.4.7-4\text{Me},4\text{Ind})_2\text{ZrCl}_2$</td>
<td>78000</td>
<td>190000</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$</td>
<td>36900</td>
<td>260000</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$</td>
<td>20200</td>
<td>320000</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Si}(2.4.7-4\text{Me},4\text{Ind})_2\text{ZrCl}_2$</td>
<td>119100</td>
<td>250000</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Si}(2.4.7-4\text{Me},4\text{Ind})_2\text{ZrCl}_2$</td>
<td>16600</td>
<td>730000</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Si}(2.4.7-4\text{Me},4\text{Ind})_2\text{ZrCl}_2$</td>
<td>15500</td>
<td>250000</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Si}(2.4.7-4\text{Me},4\text{Ind})_2\text{ZrCl}_2$</td>
<td>3300</td>
<td>18000</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Si}(2.4.7-4\text{Me},4\text{Ind})_2\text{ZrCl}_2$</td>
<td>2000</td>
<td>5000000</td>
</tr>
<tr>
<td>$\text{Cp}_2\text{TiCl}_2$</td>
<td>2800</td>
<td>630000</td>
</tr>
<tr>
<td>$\text{En}(\text{Ind})_2\text{ZrCl}_2$</td>
<td>890</td>
<td>560000</td>
</tr>
</tbody>
</table>

(a) Ethene pressure = 2.5 bar, temperature = 30°C, [metalocene] = 6.25x10$^{-4}$ mol, metalloene/MAO = 250, solvent = toluene. (b) $\text{Cp}$ = cyclopentadienyl, Me = methyl, Ind = indenyl, Ind$_x$H$_{2x}$ = tetrahydroindenyl, En = C$_5$H$_4$-Flu = fluorenyl, NmCp = neomethyl cyclopentadienyl, Bz = benzyl
Polyethylenes

Table 1 compares the polymerization of ethene by selected metallocene/methylaluminoxane catalysts [23, 24]. Generally, zirconium catalysts are more active than hafnium or titanium systems. Especially, trimethyl substituted bisindenyl systems show very high activities, exceeding the activities of 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 is formed, though a lower activity is formed. This means that chain transfer reactions are much slower in the substituted zirconocene complex. The molecular weight of metalloocene polyethylene varies in a wide range between 18 000 and 1.5 million and can be easily lowered by raising the temperature.

Figure 3. Zirconocenes with different symmetries suitable for the polymerization of olefins
metalocene/ethene ratio, or by adding small amounts of hydrogen (0.1-2 mol%). Other zirconium complexes have linked amidoﬂuorenyl ligands [25]. The molecule ar weith distrib in can b lued if or 1.1 by living polymerization using bis(phenoxymine)tiatium complexes (Fl-catalysts) or other half sandwich complexes [26, 27].

For an industrial use it can be 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 party on cataaly is fo med by ad g th metallo cn, at g th same tech cal process as for heterogeneous Ziegler-Natta catalysts (drop-in technology) [28]. By this procedure a better p ricle mn b g cn rb is p sib c ad th re is less reactor wailing.

**Polypropylenes**

By metalocene/MAO catalysts it is possible to produce different fragments of micro- to es superior as isotactic, isb or k, stereb o k sib o active, ad atactic polypropylenes in combination with MAO in toluene solution [30].

In 1987 Ewen, Jones, and Razavi [31] obtained pure sib o active pb p p en a g a Cs-sym metric [Me \(_2\)C(Flu)(Cp)]ZrCl\(_2\) cm p ex with a bi g d cyclopentadienyl and a ﬂuorenyl ring. This and other C\(_{2}\)-sym metric metallo en s of fer two different bi in n pb it in th ia n d p p en a m an alternating structure with methyl groups [32]. The selectivity in propene polymerization is an interesting task [33].

In Table 2 comparisons are made with the activities of the propene polymerization by different metalloene/MAO catalysts, the molecular weights, the isoactivities calc shed from \(^{1}H\)-NMR measured mesopentades (mmmm), the microstructure, and the melting points of the obtained polypropylenes. The activities vary between 130 and 15000 kg PP/mol Zr/h at 30°C and the molecular weights between 2000 and 750 000 g/mol. Highest isotacticity of 99% was obtained using [En(2,4,7-Me\(_2\)Ind)]ZrCl\(_2\) as cataly

**Table 2. Comparison of propene polymerization**

<table>
<thead>
<tr>
<th>Metallocene(a)</th>
<th>Activity(b)</th>
<th>Molecular weight (g/mol)</th>
<th>Isotacticity (mmmm) (%)</th>
<th>Microstructure(c)</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp,ZrCl(_2)</td>
<td>140</td>
<td>2000</td>
<td>7</td>
<td>a</td>
<td>–</td>
</tr>
<tr>
<td>(NnMcp),ZrCl(_2)</td>
<td>170</td>
<td>3000</td>
<td>23</td>
<td>sb</td>
<td>118</td>
</tr>
<tr>
<td>[En(Ind)],ZrCl(_2)</td>
<td>1 690</td>
<td>32 000</td>
<td>91</td>
<td>i</td>
<td>136</td>
</tr>
<tr>
<td>[En(Ind)],HClCl</td>
<td>610</td>
<td>446 000</td>
<td>85</td>
<td>s</td>
<td>126</td>
</tr>
<tr>
<td>[En(2,4,7Me(_2)Ind)],ZrCl(_2)</td>
<td>750</td>
<td>418 000</td>
<td>&gt;99</td>
<td>s</td>
<td>162</td>
</tr>
<tr>
<td>[Me(_2)S(Ind)],ZrCl(_2)</td>
<td>1 940</td>
<td>79 000</td>
<td>96</td>
<td>s</td>
<td>148</td>
</tr>
<tr>
<td>[Ph,S(Ind)],ZrCl(_2)</td>
<td>2 160</td>
<td>90 000</td>
<td>94</td>
<td>s</td>
<td>136</td>
</tr>
<tr>
<td>[Me(_2)S(2,4,7Me(_2)Ind)],ZrCl(_2)</td>
<td>3 800</td>
<td>192 000</td>
<td>95</td>
<td>s</td>
<td>155</td>
</tr>
<tr>
<td>[Me(_2)S(2,4,7Me(_2)Ind)],ZrCl(_2)</td>
<td>15 000</td>
<td>650 000</td>
<td>99</td>
<td>s</td>
<td>160</td>
</tr>
<tr>
<td>[Me(_2)S(2Me-4PhInd)],ZrCl(_2)</td>
<td>6 100</td>
<td>380 000</td>
<td>98</td>
<td>s</td>
<td>157</td>
</tr>
<tr>
<td>[Ph,C(Fluoro)(Cp)],ZrCl(_2)</td>
<td>1 980</td>
<td>729 000</td>
<td>0.4</td>
<td>s</td>
<td>141</td>
</tr>
<tr>
<td>[Me(_2)C(Fluoro)(Cp)],ZrCl(_2)</td>
<td>1 550</td>
<td>159 000</td>
<td>0.6</td>
<td>s</td>
<td>138</td>
</tr>
<tr>
<td>[Me(_2)C(Fluoro)(Cp)],HCl</td>
<td>130</td>
<td>750 000</td>
<td>0.7</td>
<td>s</td>
<td>138</td>
</tr>
<tr>
<td>[Me(_2)C(Fluoro)(3-4 BuCp)],ZrCl(_2)</td>
<td>1 045</td>
<td>52 000</td>
<td>89</td>
<td>s</td>
<td>130</td>
</tr>
</tbody>
</table>

(a) Propene pressure = 2 bar; temperature = 30°C; metalloene = 6.25×10\(^{-4}\) mol, metalloene/MAO = 250; solvent = 200 mL toluene; (b) Cp = cyclopentadienyl; Nn = neomenthy; Ind = indenyl; En = C\(_{2}\)H\(_{5}\); Benzld = benzoinidenyl; Flu = ﬂuorenlyl; (c) in kg PP/mol Zr/Hf.h.concentration of propene; (d) a = atactic; i = isotactic; s = syndiotactic; sb = stereoblock; ib = isoblock
component. Non-chiral ansa-metallo en s su h as [(CH₃)₂Si(Flu)]₂ZrCl₂ (Figure 3) produce atactic poly-
propylene.

**Polyolefin nanocomposites**

Polyolefin nanocomposites are of great interest because of their inherent and unique properties with respect to their mechanical, thermal and barrier properties [34]. The properties of the nanocomposites are not only influenced by the kind of fillers but also by the microstructure of the polyolefins and the preparation process. Metallocene catalysts are soluble in the presence of 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, or is 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 is added to form 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 metalloocene 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 increase in stiffness with a high gas barrier properties, significant flame retardant, better clarity, and gloss as well as high crystallization 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 p u, 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 M₉ = 1,200,000 – 1,700,000. The polymerization activity reached 5000 kg PP/mol ZrCl₂[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 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 using 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.
ated PP b still mately sepa rated from each b b r is p r meate with p n or er ad seems to b wide h 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 rese str y ad mak th s cm p ite material su tab e fo a w ap ication su h as in th at m otive plastic industries [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

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 th b n er ch in h y lw amo ns are a ed d to d crease th d n ity ad th mel ting p h of ethene copolymers. The low amount of oligomers compared to copolymers produced by Ziegler-Natta catalysis is resp ible fo a h tea ile streng h and other mechanical properties 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 they are b ain d p n ers with cry tallin polyethylene backbone chains and amorphic ethene/propene copolymer side chains.

Figure 7 shows a scheme for the preparation of in ch in b an d p y th ce b using two different metalloenes in catalysts in two steps. In a first step ethene/propene macromers were produced by a [(C₅H₄(CH₃)₂)ZrCl₂/MAO catalyst with molecular weights of 8000 to 25 000 g mol⁻¹ (Step A). The propene content varied from 13 to 23 wt%. The macromers b ain d were amo p c, sb b le in t b u o , and show a high content of vinyl end-groups. In the following copolymerization of the ethene/propene macromers with eth b , a different metalloene [Ph₂C(2,7-di-tert-Bu-Fu)(Cp)]ZrCl₂, was ed to catalyze the copolymerization (Step B). Small amounts of g n were ad ed to red e th mb mch ar weig for easier rheological measurements.

By the copolymerization of cyclic olefins such as cy l o e n b a n with eth b ad th r a-olefins are obtained cycloolefin copolymers (COC) rep eshe n g a w cla b mb mp astic, amo b materials [44, 45]. Cyclopentene, norbornene or other cyclic olefins are incorporated exclusively by 1,2-ec r in in o th g w ig cp n er ch in o rig opening occurs. The insertion of the huge norbornene monomer is very fast by metalloocene/MAO catalysts.

Table 3 compares the activities and incorporation of norbornene by different catalysts. By special conditions the polymerization rate of a 1:1 molar mixture of eth b ad n b n is h g r h b h b y-merization of ethene (comonomer effect).

The [Ph₂C(Ind)(Cp)]ZrCl₂/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>Metallocene(1a)</th>
<th>t (min)</th>
<th>Activity (kg/mol h)</th>
<th>Incorp of norbornene (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₂ZrCl₂</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>[Me₂Si(Ind)₂]ZrCl₂</td>
<td>15</td>
<td>2320</td>
<td>28.4</td>
</tr>
<tr>
<td>[En(IndH₅)₂]ZrCl₂</td>
<td>40</td>
<td>480</td>
<td>28.1</td>
</tr>
<tr>
<td>[Me₂C(Flu)(Cp)]ZrCl₂</td>
<td>10</td>
<td>7200</td>
<td>28.9</td>
</tr>
<tr>
<td>[Ph₂C(Flu)(Cp)]ZrCl₂</td>
<td>10</td>
<td>6000</td>
<td>27.3</td>
</tr>
<tr>
<td>[Ph₂C(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] = 5×10⁻⁴ mol/L, metalloocene/MAO = 200. Solvent = toluene; (b) Cp = cyclopentadienyl, Me = methyl, Ind = indenyl, En = C₅H₄, Flu = fluorenyl, Ph = phenyl

[39]
with $n$ being a, $b$ is an alternating structure, too.

Most metalloccenes produce polymers with a statistical structure, few $b$ or $d$ in the polymer with an alternating structure. Statistical copolymers are amorphous if more than 10-15 mol% of cycloolefins are incorporated in the polymer chain. The glass transition temperature can be varied with a wide range of $n$-alkanes as cycloolefin and variation of the amount in o-diphenyl ether 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 and mica b, mica d in ad -

**Polyolefins with polar comonomers**

The introduction of polar groups into polyolefins to improve processing characteristics has been an important area of research [47, 48]. It is one way to modify the properties of polymers. The functionalization of polyolefins offers a possibility to broaden applications in areas, less explored before. Only few functionalization processes are available ad -

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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, hexyl, octyl, and decyl esters with high activities after pretreatment with molybdenum(II) chloride. 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 they may be introduced. Additionally, these types of copolymers have 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 metathesis of oleic acid methyl ester. The structures are shown in Figure 8.

EXPERIMENTAL

The polymerization experiments were performed using standard Schlenk, syringe, and glovebox technique. Argon was purchased from Linde and purified by passing through an Oxisorp 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 at room temperature, and then it was 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 1.5x10−4 mol/L. The reaction was quenched by addition of 5 mL HCl ethanol. The obtained polymer was stirred over night with diluted hydrochloric acid. After phase separation, the precipitated polymer was washed three times with water and reduced to 50-70 mL at the rotary evaporator. The polymer was precipitated using ethanol, filtered off, 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 DCl (74.24 ppm).

For 'H-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. Calibrating was made using standard adamant as a standard for a phase transition. Samples were melted at 200°C, quenched from 200°C until -200°C, and heated from -200°C to 200°C, at heating rate of 20°C per min. 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 200 instrument with HT 106, 104, and 103 Å columns. The is tran eth p rate as a cm b n d refract x ad v see it y dector n t, which allow ed th calch a tion of appropriate Mark-Houwink constants for 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 from cm b t yield d in th t in a seph in c, were analyzed using an IRMS mass spectrometer. The ions w ere cep rated b sed n oth ir ch ad cm p red against mass.

### RESULTS AND DISCUSSIONS

For the polymerization of ethene and allyl ethyl ether the zirconocene [(CH₂)₅Si(Ind)₂]ZrCl₂ and MAO were used. Table 4 shows the polymerization results.

Table 4 shows that it is possible to copolymerize allyl ethyl ether with activities that are metallo catalysts. The activities are very high for low ethene concentration (79,300 kg copolymer/mol zirconocene in 1 hour) in the starting phase but decreases hardly if the co eth ratio d decreases at a th p ar metal was treated with triisobutyl aluminum (TIBA) as a complexation agent. The molecular weights of the copolymer increase with an increasing co eth ratio too. Allyl ethyl ether was incorporated with the highest value of 3.2 mol% which are about 9 wt%. The in o p atin increased when th p essn e th a was dropped to 1 bar. A copolymer with 16 mol% of AEE was obtained by using [(CH₂)₅Si(2-CH₂-4-Naph-Ind)]ZrCl₂ 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 chaimed 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 siv 1 referent to th v g p 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>
mer between 5.48 and 5.07 ppm, suggesting a complete conversion of the polar monomer. To determine the temperature effect, different temperatures of 30°C, 45°C, and 60°C were studied. The polymerization rate was found to increase with an increasing length of the monomer, especially if the amount of MAO had an influence on the polymerization activity, which was varied between 200 and 400 mg. With an increase in the MAO concentration, the catalytic activity rapidly reached its initial activity. This result was also observed for copolymerization of ethene and HBE and DBE.

In the copolymerization reactions, melting points and molar mass were determined for the copolymers. The molecular weights varied between 530,000 and 125,000. With an increase in the concentration of ethene, the molecular weight decreased. The same trend was observed for allyl propyl ether (APE) with an additional methyl group in the structure of APE. In general, at 45°C the incorporation of AEE shows a maximum.

In order to investigate the influence of a linker with an additional methyl group in the structure, allyl propyl ether (APE) was copolymerized with ethene and compared with the results for AEE. For this comparison a more bulky zirconocene such as (rac-[Me₂Si(2-Me-4-(1-Naph)Ind)]₂ZrCl₂) was used.

Surprisingly, the activities for the copolymerization with APE were higher than those for AEE. At an ethene 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 ethene concentration in the feed was higher for APE than for AEE. This result suggested that the presence of one more methylene group in the structure of APE could reduce the negative influence on the polar group on the catalytic activity. If, however, more methylene groups were present in the structure like in HBE or DBE the activities dropped again compared to AEE (see Table 4).

Figure 10 shows the dependence of the incorporation rate of ethene with its concentration for AEE and APE. The incorporation increased as expected for APE with an increasing APE concentration in the feed and reaches 8.2 mol% at 0.1 mol/L APE concentration. For AEE there appeared a maximum at an ethene concentration of 0.04 mol/L. The molecular weights of APE/ethene copolymers decreased with ethene concentration of APE and are 132°C by 2 mol%, 110 by 4.5
Figure 10. AEE and APE incorporation (wt %) into the copolymer in dependence of the ether concentration in the feed.

mol% and 95 by 8.2 mol% of APE in the copolymer.

To widen up the possibility of functionalization of \( \text{cb} \) er ers, esp cially to \( \text{h} \), a \( \text{b} \) e \( \text{f} \) b \( \text{b} \) r reactio in \( \text{cb} \) er er, etb e was ce- polymerized with 2,7-octadienyl methyl ether (MODE) by different metalloocene/MAO catalysts. In this case ag in trisb i alm in m was ed to p t ect b b u n l e t b e p p p p is a t h b u n l g r o u p from the active site during the copolymerization reaction. The obtained polymers were character- ized by GPC, elemental analysis, DSC, NMR (\(^1\)H) and FT-IR.

The yields and activities of the copolymerization of MODE with the catalyst \( \text{Me}_2\text{SiInd}_2\text{ZrCl}_2/\text{MAO} \) are shown in Table 5.

Under the investigated experimental conditions, the catalytic activity was greatly influenced by the presence of the comonomer. The effect of the reaction temp ratu e was also e d a g th e r a t o c y t a l y c activity with the p es e e b to the protected functional monomer. The catalytic activity d p d d e n t r y of th p es e d a e co entration of the polar monomer. The higher the concentra b a m er in the feed th l w er was the catalytic activity. The highest level of incorporation was 7.3 (wt %) in the presence of the cataly t s y tem \([\text{Ph}_2\text{Si(OctHF}lu(\text{Ind})]_2\text{ZrCl}_2/\text{MAO}\), fol-

Table 5. Ethene polymerization with \( \text{Me}_2\text{SiInd}_2\text{ZrCl}_2/\text{MAO} \) in the presence of MODE.a

<table>
<thead>
<tr>
<th>Run</th>
<th>( C_{\text{MODE}} ) (mol/L)</th>
<th>Temperature (°C)</th>
<th>Yields (g)</th>
<th>Activity (kg/( \text{molcat.h} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.025</td>
<td>45</td>
<td>2.9</td>
<td>509</td>
</tr>
<tr>
<td>2</td>
<td>0.03</td>
<td>45</td>
<td>1.7</td>
<td>313</td>
</tr>
<tr>
<td>3</td>
<td>0.04</td>
<td>45</td>
<td>1.6</td>
<td>304</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>45</td>
<td>0.97</td>
<td>182</td>
</tr>
<tr>
<td>5</td>
<td>0.06</td>
<td>60</td>
<td>0.59</td>
<td>114</td>
</tr>
<tr>
<td>6</td>
<td>0.015</td>
<td>60</td>
<td>0.79</td>
<td>1000</td>
</tr>
<tr>
<td>7</td>
<td>0.025</td>
<td>60</td>
<td>0.86</td>
<td>1060</td>
</tr>
<tr>
<td>8</td>
<td>0.04</td>
<td>60</td>
<td>0.34</td>
<td>406</td>
</tr>
<tr>
<td>9</td>
<td>0.05</td>
<td>60</td>
<td>0.28</td>
<td>326</td>
</tr>
</tbody>
</table>

aPolymerization conditions: ethene pressure 4bar, toluene volume 200mL, polymerization time 1h, \([\text{Me}_2\text{Si(Ind)}]_2\text{ZrCl}_2 = 3\times10^{-4}\text{mol/L}\), cocatalyst 400 mg MAO; MODE/TIBA = 1:1, precontacted for 30 min.

The physical properties (melting point, molecular weight and polydispersity index) of the obtained polymers are summarized in Table 6.

The physical properties of the copolymers seem to be temperature dependent. At 45°C, it is clearly obser b a d e crease trend in b h m c e a r w e ad melting point with increase in comonomer in feed. Comparing the results with the reaction at 60°C, the cb er e d s b a s m e t e l b h i v d a s at 45°C with systematically lower \( T_m \) in reas e in polar monomer feed. The polydispersity index was about 3 with an increase in the concentration of feed polar group.

Additionally, it was observed that there was not strg d p d c e n th meltig p h b o the b -tained polymer with the polymerization temperature. However, at the same concentration of the polar...
The development of metalloocene/methylaluminoxane catalyts have strig y in reased th w leg the olefin polymerization catalysts. This knowledge has made it possible to find new bulky and weakly coordinating cocatalysts such as perfluorophenyl-borate anions and boranes. The development is not comp eted for w tran itin metal cm p act by MAO or other cocatalysts. It would be an important step to decrease the amount of MAO, needed for the activation. Supporting the methylaluminoxane on silica, alm in o w g c b ers cb d b one way for this.

Figure 11. $^1$H-NMR spectrum of a MODE/ethene copolymer

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 metallo c sed b ers from th cataly t struc ture allow s th md lig b their reaction kinetics and the polymerization process [50]. Reactor models could be developed using mass ad c g b lan es ad y d scrib th b b er cm p itin as well as reacto p ratig cd ti , required for a given polymer architectures. It would be possible to design polyolefins with tailored molecular weight, cm er cb ch , lb and sh t ch in branching [51], and comonomer distribution independent and controlled. Morphology control is possible by suspension, cascade or multizone reactors improving melt viscosity and processing.

Polyolefin nanocomposites open up the approach to w classes b materials with g eat p party cm b assignments. A soft polyolefin matrix can be combined with h rd in g c p rticles o strg lay rs b silicates or graphene or with fibers of 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 metalloocene/MAO or other single site catalysts. Materials with h g b brrier resistan c, h th rmal ad electric cd t ty, ad h b fo m stab lity can b 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 catalyze to membrane, elastomer, and 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 as acrylic, carboxyl, ether, ester, siloxy, or amino groups. In this work, the synthesis of polyolefins with polar comonomers [52, 53].

The development and commercialization of metalloocene/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.

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