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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, polymer structure, tacticity and special properties with high precision. 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 and propene with short and long chained α-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 triisobutyl aluminum as protecting agents. Polar monomers could be incorporated into the polymer chain by up to 16 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 polar polymers 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

CONTENT

INTRODUCTION

In comparison to Ziegler-Natta systems, metallocene catalysts are soluble in hydrocarbons; show only one type of active site and their chemical structure can be easily changed. These qualities would allow to predict the properties of the resulting polyolefins accurately by knowing the structure of the metallocenes used during their synthetic process and to control the resulting molecular weight and distribution, comonomer content and tacticity by selection of the appropriate reactor

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conditions. In addition, their catalytic activity is about 100 times higher than the classical Ziegler-Natta systems. Metallocenes in combination with conventional aluminum alkyl cocatalysts, are indeed capable of polymerizing ethene, but only at a very low activity. With the discovery and application of methylaluminoxane (MAO) it was possible to enhance the activity, surprisingly, by a factor of 10,000. Therefore, MAO plays a crucial part in the catalysis with metallocenes [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 have been investigating on side reactions, especially the hydrogen transfer in homogeneous Ziegler-Natta systems [2]. To lower the reduction rate of the titanium system, we have been investigating on the reaction between biscyclopentadienyl-titanium dimethyl and trimethylaluminum, instead of a titanium-diethyl and triethyaluminum containing system mainly by NMR analysis at low temperatures. The formation of new CH_2-bridged titanium aluminum complexes is observed by a slow α-hydrogen transfer (Equation 1).

$$Cp_2Ti(CH_3)_2 + Al(CH_3)_3 \rightarrow Cp_2(CH_3)Ti\text{-}CH_2\text{-}Al(CH_3)_2 + CH_4 \qquad (1)$$

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 halogen free $Cp_2Ti(CH_3)_2$/$Al(CH_3)_3$ /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 trimethyaluminum (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.

$$nH_2O + (n + 1)\ Al(CH_3)_3 \rightarrow (H_3C)_2Al\text{-}[O\text{–}AlCH_3]_n\text{–}CH_3 + 2n\ CH_4 \qquad (2)$$

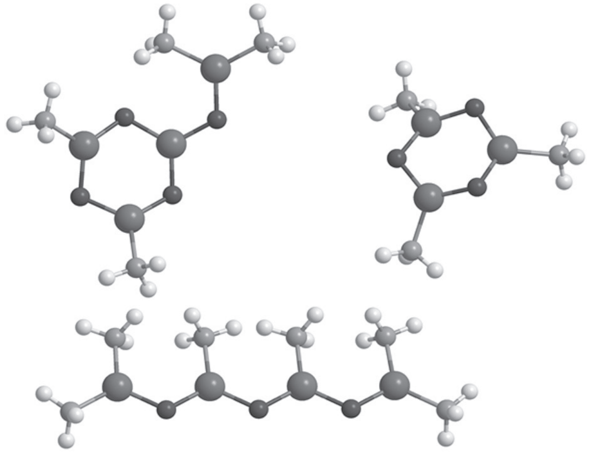


Figure 1. Structures of cyclic and linear MAO, big balls: aluminium, small balls: oxygen, and methyl groups

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 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).

Even today the exact structure is not known, because there are equilibria with the oligomers, complexation of the oligomers towards each other and the unreacted TMA. MAO is a compound in which aluminum and oxygen atoms are arranged alternately and free valences are saturated by methyl substituents. Sinn [7], Eilertsen, Rytter, and Ystenes [8] and others calculated a ratio $CH_3/Al = 1.5$ for MAO.

As the aluminum atoms in the unit structures of MAO are coordinatively unsaturated, the units join together forming clusters and cages. These have molecular weights from 1200 to 1600, measured by cryoscopy in benzene and are soluble in hydrocarbons especially in aromatic solvents. A probable association and cage like structure of four $[Al_4O_3Me_6]$ units 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 alkylation of the metallocene complex in case that a dichloride is used. The other is the formation of an ion-pair. Marks [9], and Bochmann [10], showed that the activity of metallocene catalysts depends on the formation of cationic species. Today, most research groups agree with this statement. The bulky MAO

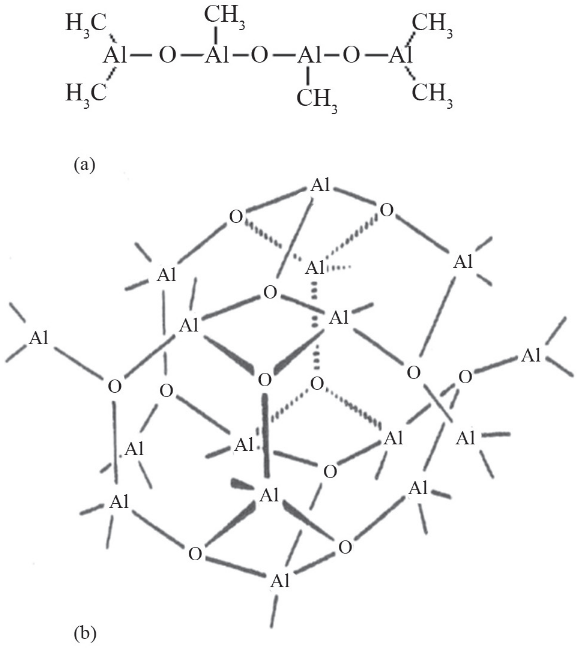


Figure 2. a: Unit structure of MAO, b: cage formed by four linear unit structures with four and six- membered rings

cluster takes a chlorine-atom or a methyl-group from the metallocene together with an electron forming a cationic metallocene and an anionic MAO complex (Equation 3)

$$Cp_2Zr(CH_3)Cl + MAO \rightarrow [Cp_2Zr(CH_3)]^+ + [MAO\text{-}Cl]^- \qquad (3)$$

Essential to polymerization activity would be the formation of bulky anions with a weak bonding to the metallocene cations. Knowing that the bulky structure of MAO could be necessary for the activation of metallocene catalysts, the bulky and weakly coordinating cocatalysts such as tris(pentafluorophenyl)borane or organic salts of the tetrakis (pentafluorophenyl) borate $[(C_6F_5)4B]^-$, and aluminum fluorides were introduced [9, 10]. With these cocatalysts a metallocene/cocatalysts ratio of 1:1 was used but only when a high excess of an aluminum alkyl as scavenger was present.

The polyolefin industries have used MAO containing catalysts in a large scale. Currently, companies such as Albermale, Akzo, Chemtura, and Mitsui produce hundreds of tons of MAO by reaction of water or ice with trimethylaluminum and in some cases add other aluminum alkyls to increase their solubility.

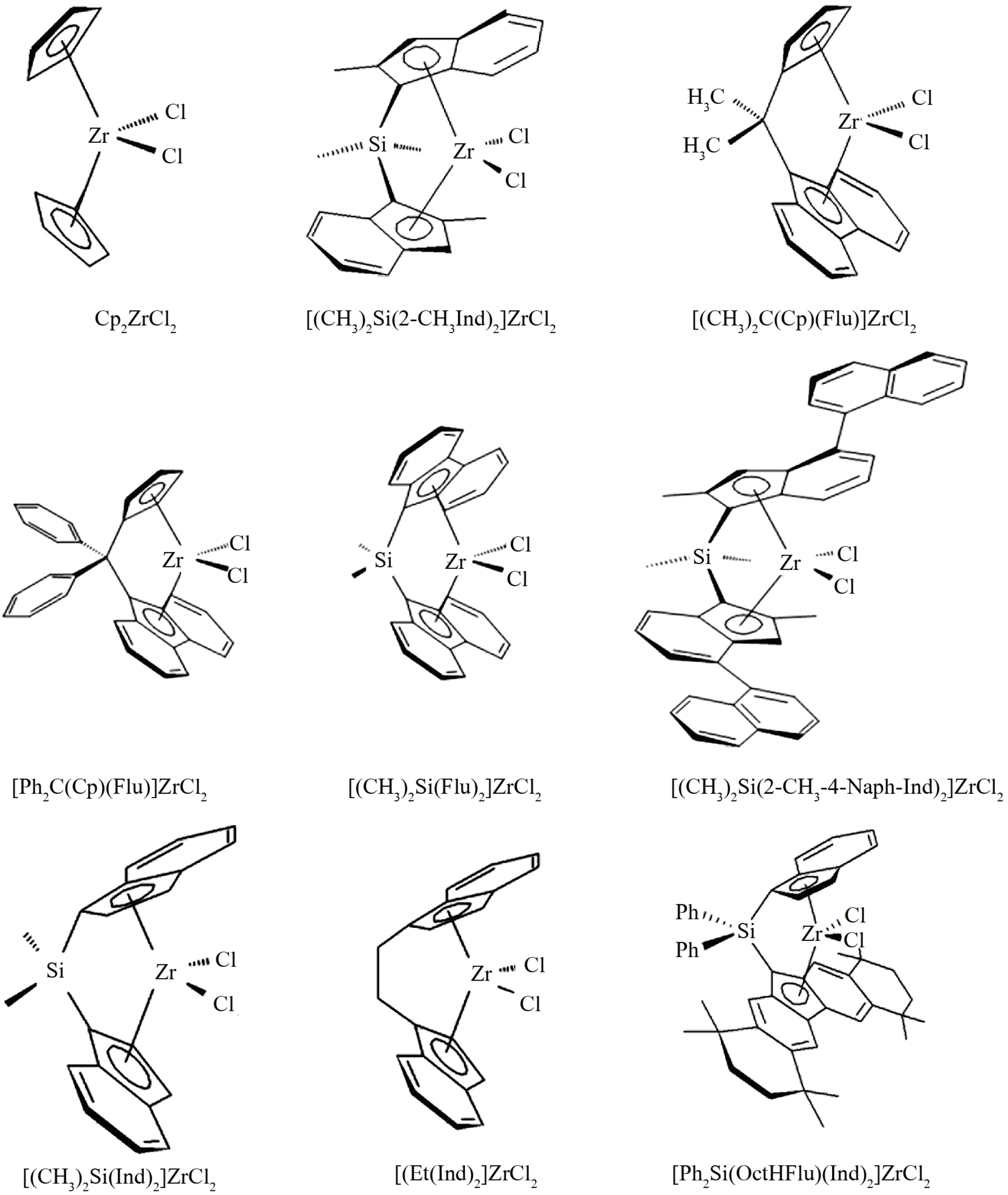
Homo-polyolefins

Metallocenes, 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 worldwide research groups to thousands of patents and publications in the last 20 years. An overview can be found in selected review articles and books [11-20]. It could be shown that a soluble catalyst, such as Cp_2ZrCl_2/MAO is able to produce polyethylene with high molecular weights and a narrow molecular weight distribution of approximately two. All active sites are similar and form polymers with the same average chain length (single site catalysts). Only traces of low molecular weight oligomers are formed. Zirconocenes with different symmetries and substitutions are shown in Figure 3. There is a great variety of the structure of metallocenes, which can be used for the polymerization. The cyclopentadienyl-, indenyl-, fluorenyl- ligands could be hydrated or substituted by alkyl, aryl, methoxy, siloxy or other groups. Ethanediyl (C_2H_4), dimethylsilandiyl ($(CH_3)_2Si$), or isopropandiyl ($(CH_3)_2C$) are mainly used as interannular bridges between the rings [21]. Central metals could be Ti, Zr, Hf. Such and similar metallocenes are used for the polymerization of ethene, propene, and other olefins [22].

Table 1. Comparison of ethene polymerization $^{(a)}$ with different metallocene/methylaluminoxane catalysts at same polymerization conditions

Metallocene$^{(b)}$ (Met)	Activity [kg PE/ (mol Met×h×c_E)]	Molecular weight (g/mol)
Cp_2TiCl_2	34200	400000
Cp_2ZrCl_2	60900	620000
Cp_2HfCl_2	4200	700000
$Cp^*_2ZrCl_2$	1300	1500000
$En(IndH_4)_2]ZrCl_2$	22200	1000000
$[En(Ind)_2]ZrCl_2$	12000	350000
$[En(Ind)_2]HfCl_2$	2900	480000
$[En(2,4,7\text{-}Me_3Ind)_2]ZrCl_2$	78000	190000
$[Me_2Si(Ind)_2]ZrCl_2$	36900	260000
$[Ph_2Si(Ind)_2]ZrCl_2$	20200	320000
$[Me_2Si(2,4,7\text{-}Me_3Ind)_2]ZrCl_2$	111900	250000
$[Me_2Si(2Me\text{-}4Ph\text{-}Ind)_2]ZrCl_2$	16600	730000
$[Me_2C(Ind)(Cp)]ZrCl_2$	15500	25000
$[Ph_2C(Ind)(Cp)]ZrCl_2$	3300	18000
$[Me_2C(Flu)(Cp)]ZrCl_2$	2000	500000
$[Ph_2C(Flu)(Cp)]ZrCl_2$	2800	630000
$[Me_2C(Flu)(Cp)]HfCl_2$	890	560000

(a) Ethene pressure = 2.5 bar, temperature. = 30°C, [metallocene] = $6,25x10^{-6}$ mol, metallocene/MAO = 250, solvent = toluene , (b) Cp = cyclopentadienyl, Me = methyl, Ind = indenyl, $IndH_4$ = tetrahydroindenyl, En = C_2H_4, Flu = fluorenyl, NmCp = neomenthyl cyclopentadienyl, Bz = benzyl



Cp_2ZrCl_2 $[(CH_3)_2Si(2\text{-}CH_3Ind)_2]ZrCl_2$ $[(CH_3)_2C(Cp)(Flu)]ZrCl_2$

$[Ph_2C(Cp)(Flu)]ZrCl_2$ $[(CH_3)_2Si(Flu)_2]ZrCl_2$ $[(CH_3)_2Si(2\text{-}CH_3\text{-}4\text{-}Naph\text{-}Ind)_2]ZrCl_2$

$[(CH_3)_2Si(Ind)_2]ZrCl_2$ $[(Et(Ind)_2]ZrCl_2$ $[Ph_2Si(OctHFlu)(Ind)_2]ZrCl_2$

Figure 3. Zirconocenes with different symmetries suitable for the polymerization of olefins

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 those of sterically less hindered Cp_2ZrCl_2. When pentamethyl cyclopenta - dienyl - zirconium dichloride ($Cp^*_2ZrCl_2$/MAO) is used instead of Cp_2ZrCl_2/MAO, a polyethylene of much higher molecular weight, though a lower activity is formed. This means that chain transfer reactions are much slower in this substituted zirconocene complex. The molecular weight of metallocene polyethylenes varies in a wide range between 18 000 and 1.5 million and can be easily lowered by increasing the temperature, raising the metallocene/ethene ratio, or by adding small amounts of hydrogen (0.1-2 mol%). Other zirconium complexes have linked amidofluorenyl ligands [25]. The molecular weight distribution can be lowered down to 1.1 by living polymerization using bis(phenoxy-imine)titanium complexes (FI-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 heterogeneous catalyst is formed by adding the metallocene, adopting the same technical process as for heterogeneous Ziegler-Natta catalysts (drop-in technology) [28]. By this procedure a better particle morphology control is possible and there is less reactor walling.

Polypropylenes

By metallocene/MAO catalysts it is possible to produce different kinds of microstructures such as isotactic, isoblock, stereoblock, syndiotactic, and atactic polypropylenes in high purity (Figure 4). It was shown in 1984 that with chiral *ansa*-metallocenes, firstly isolated by Brintzinger [29], that a highly isotactic polypropylene in combination with MAO in toluene solution [30] was produced.

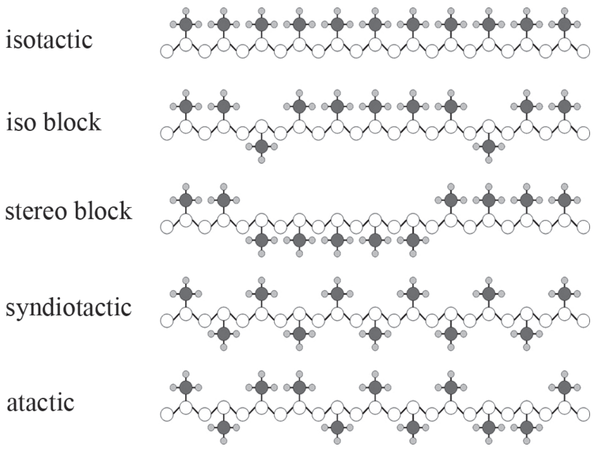


Figure 4. Microstructures of polypropylenes obtained by various metallocene catalysts (hydrogen atoms of the backbone chain are not shown)

In 1987 Ewen, Jones, and Razavi [31] obtained pure syndiotactic polypropylene using a Cs-symmetric $[Me_2C(Flu)(Cp)]ZrCl_2$ complex with a bridged cyclopentadienyl and a fluorenyl ring. This and other C_s-symmetric metallocenes offer two different bonding positions for the inserted propylene and form 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 metallocene/MAO catalysts, the molecular weights, the isotacticities calculated from the ^{13}C-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 2.000 and 750.000 g/mol. Highest isotacticity of 99 % was obtained using $[En(2,4,7\text{-}Me_3Ind)_2]ZrCl_2$ as catalyst

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

Metallocene(b)	Activity(c)	Molecular weight (g/mol)	Isotactacticity mmmm (%)	Microstructure(d)	Melting point (°C)
Cp_2ZrCl_2	140	2 000	7	a	–
$(NmCp)_2ZrCl_2$	170	3 000	23	sb	118
$[En(Ind)_2]ZrCl_2$	1 690	32 000	91	i	136
$[En(Ind)_2]HfCl_2$	610	446 000	85	ib	126
$[En(2,4,7Me_3Ind)_2]ZrCl_2$	750	418 000	>99	i	162
$[Me_2Si(Ind)_2]ZrCl_2$	1 940	79 000	96	i	148
$[Ph_2Si(Ind)_2]ZrCl_2$	2 160	90 000	96	i	136
$[Me_2Si(2,4,7Me_3Ind)_2]ZrCl_2$	3 800	192 000	95	i	155
$[Me_2Si(2Me\text{-}4PhInd)_2]ZrCl_2$	15 000	650 000	99	i	160
$[Me_2Si(2Me\text{-}4,5\text{-}BenzInd)_2]ZrCl_2$	6 100	380 000	98	i	157
$[Ph_2C(Fluo)(Cp)]ZrCl_2$	1 980	729 000	0.4	s	141
$[Me_2C(Fluo)(Cp)]ZrCl_2$	1 550	159 000	0.6	s	138
$[Me_2C(Fluo)(Cp)]HfCl_2$	130	750 000	0.7	s	138
$[Me_2C(Fluo)(3\text{-}t\text{-}BuCp)]ZrCl_2$	1 045	52 000	89	ib	130

(a) Propene pressure = 2 bar; temperature = 30°C; metallocene = 6.25×10^{-6} mol, metallocene/MAO = 250; solvent = 200 mL toluene; (b) Cp = cyclopentadienyl; Nm = neomenthyl; Ind = indenyl; En = C_2H_4; BenzInd = benzoindenyl; Flu = fluorenyl; (c) in kg PP/(mol Zr/Hf.h.concentration of propene; (d) a = atactic; i = isotactic; s = syndiotactic; sb = stereoblock; ib = isoblock

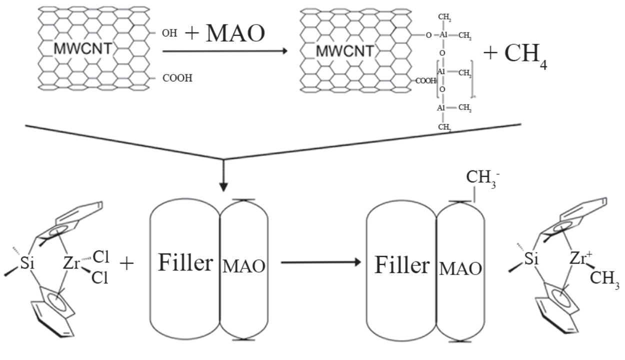


Figure 5. Formation of polymerization active sites by absorption of MAO on oxidized multiwall carbon nanotubes (MWCNT) followed by adding a zirconocene

component. Non-chiral *ansa*-metallocenes such as $[(CH_3)_2Si(Flu)_2]ZrCl_2$ (Figure 3) produce atactic polypropylene.

Polyolefin nanocomposites

Polyolefin nanocomposites are of great interest because of their high potential as materials with novel 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 hydrocarbons and can be adsorbed or anchored on 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 or is physically absorbed at the surface (Figure 5). Methane is formed by the chemical reaction of MAO with polar groups.

Excess MAO is washed out. In a second step, the metallocene is added forming 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 metallocene 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 improved stiffness with a negligible loss of impact strength, 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 $[(CH_3)_2Si(2\text{-}CH_3\text{-}4\text{-}Nap\text{-}Ind)_2]ZrCl_2$ and propene, 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 M_w = 1,200,000 – 1,700,000. The polymerization activity reached 5000 kg PP/mol Zr.h.[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 dried polypropylene nanocomposites were obtained 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 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 20nm and the thickness of the iPP coat is about 8nm. Even the loose network of polymer layered nanotubes on the lower left side, which are partially conglomer-

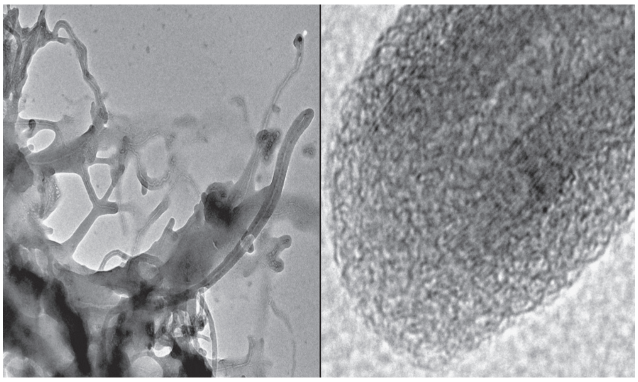


Figure 6. TEM micrographs of a MWCNT composite prepared by in-situ polymerization covered by iPP (left), top of a nanotube/iPP composite by higher resolution (right)

ated by PP but still mostly separated from each other is permeated with polymer and seems to be widening 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 increase strongly and make this composite material suitable for new applications such as in the automotive plastic industries [39].

Copolymers

Metallocene/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	(COC)
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 metallocene catalysts are characterized by a narrow molecular weight distribution of 2 and a uniform microstructure. While the comonomers are distributed randomly in the polymer chain, only low amounts are needed to decrease the density and the melting point of ethene copolymers. The low amount of oligomers compared to copolymers produced by Ziegler-Natta catalysts is responsible for a high tensile strength 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 there are obtained polymers with crystalline polyethylene backbone chains and amorphic ethene/propene copolymer side chains.

Figure 7 shows a scheme for the preparation of long-chain branched polyethylene by using two different metallocene catalysts in two steps. In a first step ethene/propene macromers were produced by a $[(C_5(CH_3)_5]_2ZrCl_2$/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 obtained were amorphic, soluble in toluene, and show a high content of vinyl end-groups. In the following copolymerization of the ethene/propene macromers with ethene, a different metallocene $[Ph_2C(2,7\text{-di-tert-}Bu_2Flu)(Cp)]ZrCl_2$ was used to catalyze the copolymerization (Step B). Small amounts of hydrogen were added to reduce the molecular weight for easier rheological measurements.

By the copolymerization of cyclic olefins such as cyclopentene or norbornene with ethene and other α-olefins are obtained cycloolefin copolymers (COC) representing a new class of thermoplastic, amorphous materials [44, 45]. Cyclopentene, norbornene or other cyclic olefins are incorporated exclusively by 1,2-insertion into the growing copolymer chain, no ring opening occurs. The insertion of the huge norbornene monomer is very fast by metallocene/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 ethene and norbornene is higher than the homopolymerization of ethene (comonomer effect).

The $[Ph_2C(Ind)(Cp)]ZrCl_2$/MAO catalyst shows not only high activities for the copolymerization of ethene

Table 3. Copolymerization $^{(a)}$ of norbornene (N) and ethene by different metallocene/MAO-catalysts

Metallocene $^{(b)}$	t (min)	Activity (kg/mol h)	Incorp of norbornene (weight %)
Cp_2ZrCl_2	30	1200	21.4
$[En(Ind)_2]ZrCl_2$	10	9120	26.1
$[Me_2Si(Ind)_2]ZrCl_2$	15	2320	28.4
$[En(IndH_4)_2]ZrCl_2$	40	480	28.1
$[Me_2C(Flu)(Cp)]ZrCl_2$	10	7200	28.9
$[Ph_2C(Flu)(Cp)]ZrCl_2$	10	6000	27.3
$[Ph_2C(Ind)(Cp)]ZrCl_2$	15	2950	33.3

Ethene pressure = 2 bar, [N] = 0.05 mol/L, temperature. = 30°C, [metallocene] = 5x10^{-6}mol/L, metallocene/MAO = 200, Solvent = toluene ; (b) Cp = cyclopentadienyl, Me = methyl, Ind = indenyl, En = C_2H_4, Flu = fluorenyl, Ph = phenyl

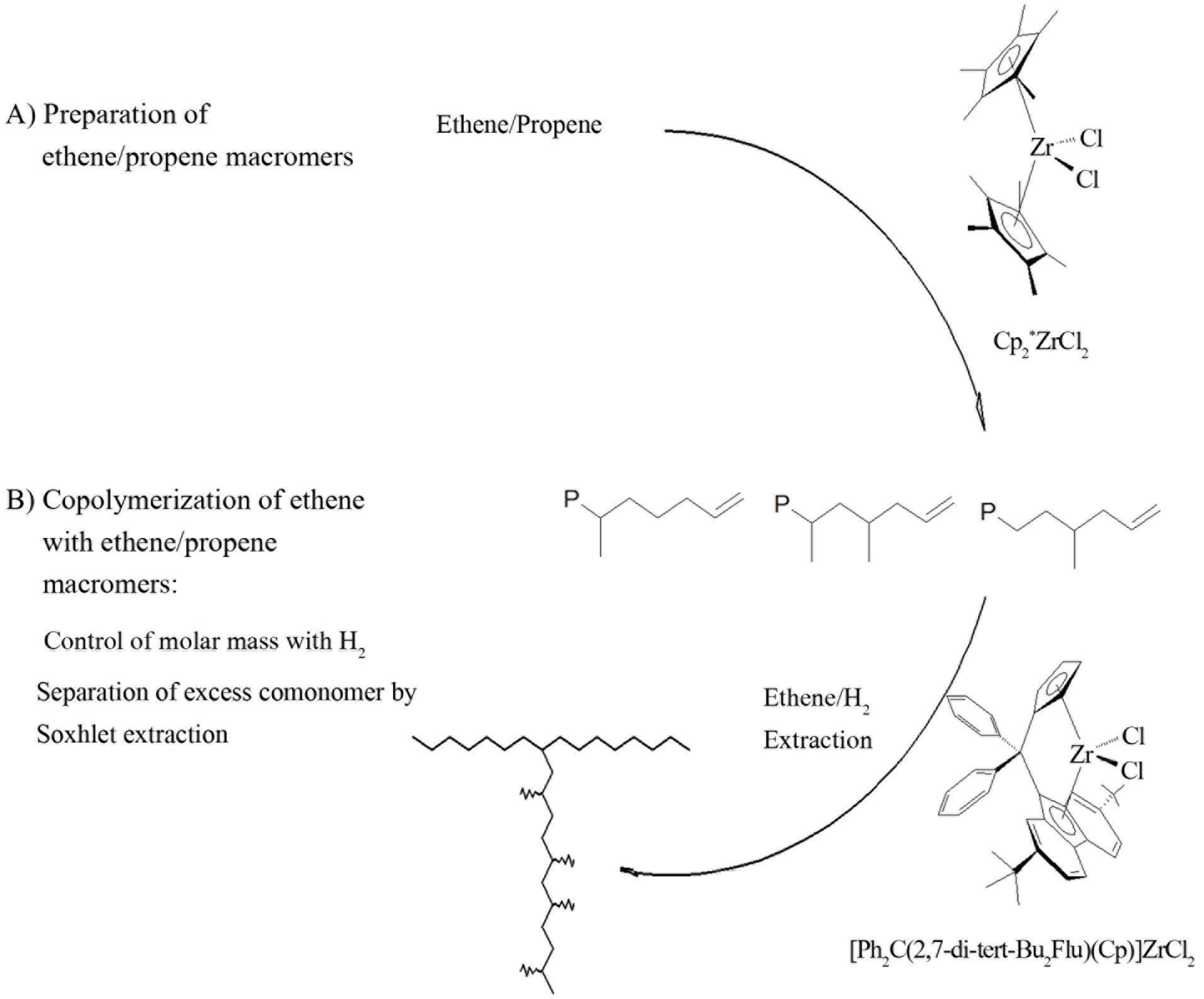


Figure 7. Reaction scheme for ethene-graft ethene/propene copolymers by two different zirconocene/MAO catalysts in two steps

with norbornene, but gives an alternating structure, too.

Most metallocenes produce polymers with a statistical structure, few others produce polymers 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 over a wide range by selection of norbornene as cycloolefin and variation of the amount of norbornene incorporated into 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 hydrolysis and chemical degradation, in combination with their stiffness makes them interesting materials for optical applications, for example in compact discs, lenses, optical fibers, or films [46]. Meanwhile, ethene-norbornene COC-materials are commercially produced.

Polyolefins with polar comonomers

The introduction of polar groups into polyolefins to improve processing characteristics and other properties of the polymers is nowadays one of the most important areas for both academic and industrial research[47, 48]. It is one way to modify the properties of a polymer, because these functional groups control important polymer properties such as adhesion, barrier and surface properties, solvent resistance, miscibility with other polymers, and rheological properties. The functionalization of polyolefins offers a possibility to broad applications in areas, less explored before. Only few functionalization processes are available and the obtained copolymers have not a uniform structure. Metallocene and other single site catalysts are able to polymerize ethene and polar vinyl monomers, such as, ethers, alcohols, and esters with high activities after protection of the functional groups and these copolymers have a uniform structure [49]. 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 both ionic and chemical cross links may be introduced. Additionally, these types of copolymers have excellent dyeing properties, good permeability of gaseous materials and weather-proof functions 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 metathesis of oleic acid methyl ester. The structures are shown in Figure 8.

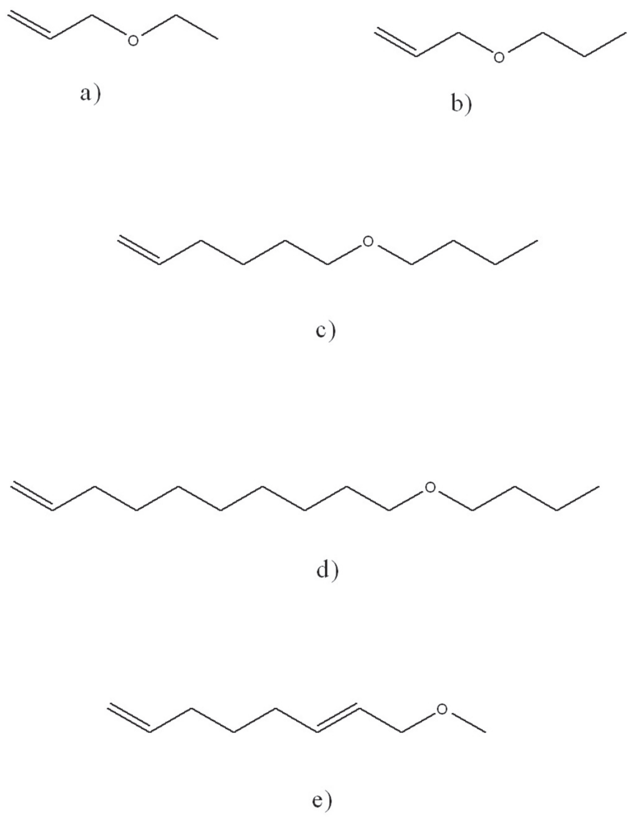


Figure 8. Structure of in this work used vinyl ethers. (a) allyl ethyl ether (AEE), (b) allyl propyl ether (APE), (c) hexcenyl butyl ether (HBE), (d) decenyl butyl ether (DBE), (e) 2,7-octadienyl methyl ether (MODE)

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 3Å molecular sieve. A solution in toluene (1mol/L) of the different vinyl ethers was dried over molecular sieves for 48 h and stored under argon atmosphere and then it was stirred for 3 h with triiso-butylaluminium (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^{-6}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 organic phase 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 ^{13}C-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 referenced to $C_2D_2Cl_4$ (d 74.24 ppm).

For ^{1}H-NMR, the samples were prepared by dissolving 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. Calibration was made using indium for the enthalpy standards and n-octane as a standard for peak temperature 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 GPCV 2000 instrument with HT 106, 104, and 103 Å columns. The instrument operated with a combined refractive index and viscosity detector unit, which allowed the calculation 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 after combustion yielded ions that in a step further, were analyzed using an IRMS mass spectrometer. The ions were separated based on their charge and compared against mass.

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 ethers with good activities by metallocene catalysts. The activities are very high for low ether concentration (79,300 kg copolymer/mol zirconocene in 1 hour) in the starting phase but decreases hardly if the concentration decreases although the polar monomer was treated with triisobutyl aluminum (TIBA) as a complexation agent. The molecular weights of the copolymers decrease with an increasing concentration, 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 droped to 1 bar. A copolymer with 16 mol% of AEE was obtained by using $[(CH_3)_2Si(2\text{-}CH_3\text{-}4\text{-}Naph\text{-}Ind)_2]ZrCl_2$ 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 chained 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 the vinyl group of the polar mono-

Table 4. Copolymerization of ethene with AEE, HBE, and DBE by 4 bar ethene pressure, 60°C, 400 mg MAO, 200 ml toluene, $[Me_2Si(Ind)_2]ZrCl_2 = 5x10^{-6}mol/L$, Al/Zr = 2 500, activity: kgPE/molZr.h

Comonomer	Concentration (mol/L)	Activity	Molecular weight (g/mol)	Incorporation (mol%)	Melting point (°C)
AEE	0.02	5 000	530 000	1.1	123
AEE	0.04	3 500	450 000	2.0	110
AEE	0.05	1 600	420 000	3.2	108
HBE	0.01	54 600	194 000	0.14	139
HBE	0.025	1 400	105 000	0.60	132
DBE	0.01	79 300	117 000	0.1	137
DBE	0.02	3 760	125 000	0.3	131
DBE	0.03	2 440	130 000	0.3	132
DBE	0.05	540	346 000	0.6	126

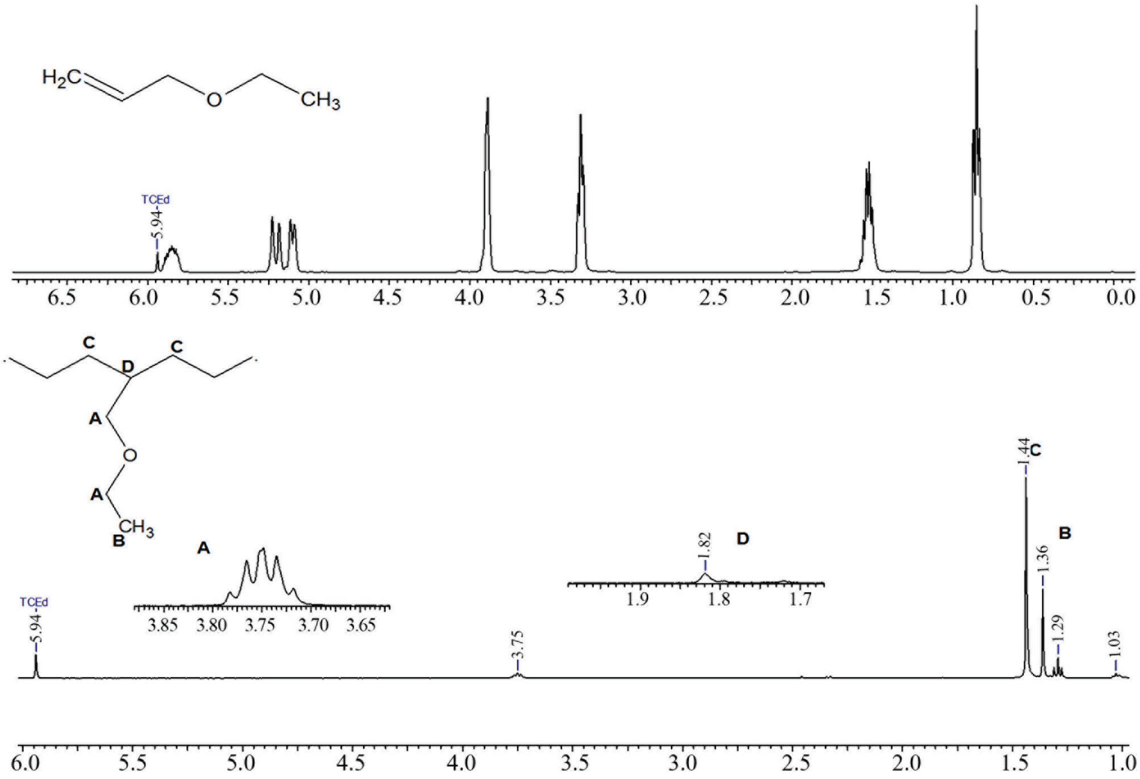


Figure 9. ^{1}H-NMR spectra of allyl ethyl ether (AEE) monomer (top) and AEE/ethene copolymer (down A,B,C)

mer between 5.48 and 5.07 ppm, suggesting a complete conversion of the polar monomer. To determine the temperature effect, experiments by temperatures of 30°C, 45°C, and 60°C were studied. The polymerization rate was the highest by the highest temperature, but the incorporation of the polar monomer was less, 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 approximately twofold of its initial activity. This result was also observed for the copolymerization of ethene and HBE and DBE.

Incorporation rates, melting points and molecular weights strongly depended on the temperature of the reaction. The molecular weights varied between 530,000 and 125,000. With an increase of the comonomer the molecular weight decreased. The same trend was observed with an increasing length of the alkyl group of the vinyl ether. In general, at 45 °C the incorporation of AEE shows a maximum.

In order to investigate the rule of an ether with an additional methylene group after the oxygen atom, 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-[$Me_2Si(2\text{-}Me\text{-}4\text{-}(1\text{-}Naph)Ind)_2]ZrCl_2$) 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 that for AEE. This result suggested that the presence of one more methylene group in the ether 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 ether 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 the ether with its dependence the ether 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 of the incorporation rate at an ether concentration of 0.04 mol/L. The molecular weights of APE/ethene copolymers decreased with the incorporation rate of APE and are 132°C by 2 mol%, 110 by 4.5

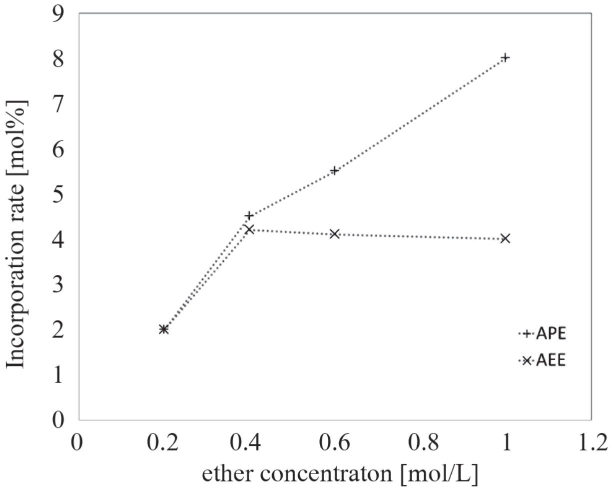


Figure 10. AEE and APE incorporation (wt %) into the copolymer in dependence of the ether concentration in the feed

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

To widen up the possibility of functionalization of copolymers, especially to have a double bonds for other reactions in the copolymer, ethene was copolymerized with 2,7-octadienyl methyl ether (MODE) by different metallocene/MAO catalysts. In this case again triisobutylaluminium was used to protect the functional ether group by insulating the functional group from the active site during the copolymerization reaction. The obtained polymers were characterized by GPC, elemental analysis, DSC, NMR (^{13}C and ^{1}H) and FT-IR.

The yields and activities of the copolymerization of MODE with the catalyst $Me_2SiInd_2ZrCl_2$/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 temperature was also observed using the same catalyst system. An increase in the polymerization temperature caused a decrease in the catalytic activity. The catalyst activity at 45°C, at the same MODE concentration in feed (runs 1 and 2), was 1 order of magnitude higher than the catalyst activity of the reaction at 60°C. However, in both temperatures studied, it was observed a decrease in the catalytic activity with the presence of the protected functional monomer. The catalytic activity depended extremely on the presence and concentration of the polar monomer. The higher the concentration of the polar monomer in the feed, the lower was the catalyst activity. The highest level of incorporation was 7.3 (wt %) in the presence of the catalyst system $[Ph_2Si(OctHFlu)(Ind)]ZrCl_2$/MAO, followed by the catalyst system $[(CH_3)_2Si(Ind)_2]ZrCl_2$/MAO with 7.1 (wt %).

Table 5. Ethene polymerization with $Me_2SiInd_2ZrCl_2$/MAO in the presence of MODE^x

Run	C_{MODE} (mol/L)	Temperature (°C)	Yields (g)	Activity (kg_{Pol}/ $mol_{cat}.h.C_{monomers}$)
1	0.025	45	2.9	509
2	0.03	45	1.7	313
3	0.04	45	1.6	304
4	0.05	45	0.97	182
5	0.06	60	0.59	114
6	0.015	60	0.79	1000
7	0.025	60	0.86	1060
8	0.04	60	0.34	406
9	0.05	60	0.28	326

^{x}Polymerization conditions: ethene pressure 4bar, toluene volume 200mL, polymerization time 1h, $[Me_2Si(Ind)_2]ZrCl_2 = 3x10^{-6}$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 the Table 6.

The physical properties of the copolymers seem to be temperature dependent. At 45°C, it is clearly observed a decrease trend in both molecular weight and melting point with increase in comonomer in feed. Comparing the results with the reaction at 60°C, the copolymer displayed the same melting point behavior as at 45°C with systematically lower T_m with increase 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 strong dependence on the melting point of the obtained polymer with the polymerization temperature. However, at the same concentration of the polar

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

Run	C_{MODE}(mol/L)	T_m (°C)	ΔH (J/g)	M_w (Kg/mol)
6	0.04	133	121	182
7	0.06	136	123	161
8	0.10	117	122	157
9	0.13	n.d.	n.d.	n.d.
1	0.07	141	152	108
2	0.08	134	148	102
3	0.10	132	148	75
4	0.13	131	126	113
5	0.15	128	n.d.	n.d.

Polymerization conditions: ethene pressure 4bar, toluene volume 200mL, polymerization time 1h, cocatalyst MAO; MODE/TIBA precontacted for 30 min. C_{MODE}: concentration in feed, T_m = melting point, ΔH= melting enthalpy, n.d. = not detected

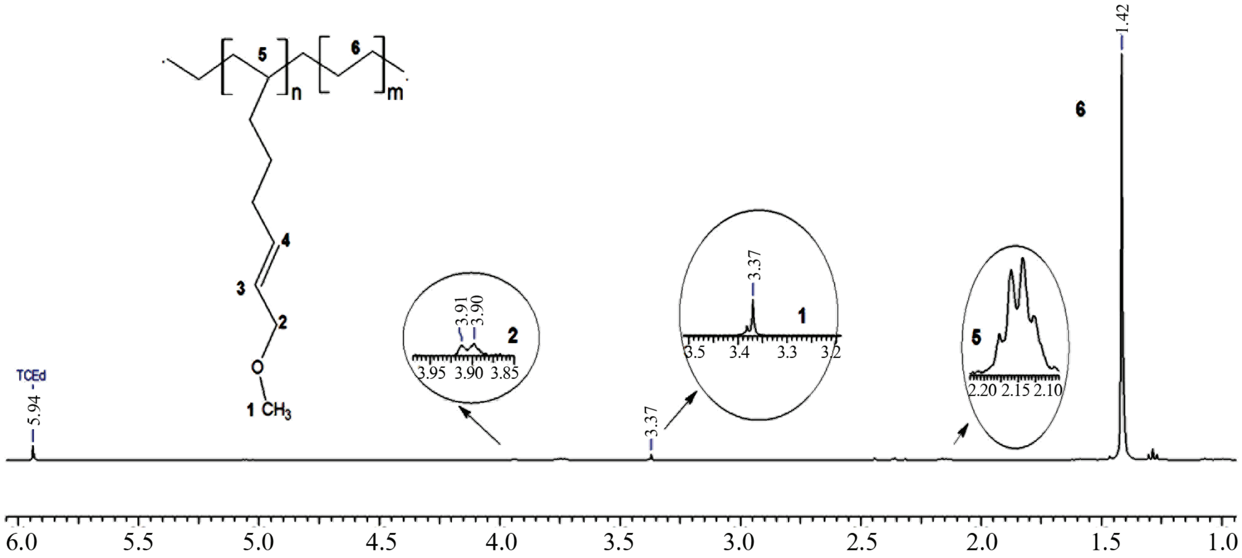


Figure 11. ^{1}H-NMR spectrum of a MODE/ethene copolymer

monomer in the feed, the melting point was higher at higher polymerization temperatures. A decrease in the molecular weight of the obtained copolymers was observed at the same time.

A preliminary ^{1}H NMR of the obtained polymer, Figure 11, shows a presence of peaks that are con sistent with MODE incorporation δ=3,37ppm (CH_3-; methyl group) and δ=3,93ppm (CH_2-O; methylene group) , this effect was confirmed by ^{13}C NMR.

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 7.1wt% (run 4, in Table 6). This high incorporation rate of a bulky polar monomer with a middle standing double bond was considered a key for further investigations with such a copolymer.

CONCLUSION

The development of metallocene/methylaluminoxane catalysts have strongly increased the knowledge of the olefin polymerization catalysis. This knowledge has made it possible to find new bulky and weakly coordinating cocatalysts such as perfluorophenyl-borate anions and boranes. The developement is not completed for new transition metal complexes activated 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, alumina or on new organic polymers could be one way for this.

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 known dependence of metallocene based polymers from the catalyst structure allows the modeling of their reaction kinetics and the polymerization process [50]. Reactor models could be developed using mass and energy balances and they describe the polymer composition as well as reactor operating conditions, required for a given polymer architectures. It would be possible to design polyolefins with tailored molecular weight, comonomer content, long and short chain 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 new classes of materials with great property combinations. A soft polyolefin matrix can be combined with hard inorganic particles or strong layers of 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 metallocene/MAO or other single site catalysts. Materials with high gas barrier resistance, high thermal and electric conductivity, and high form 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 copolymers. To design three dimensional crystallizing polyolefins for materials with special properties such as cages for catalysts or membranes, elastomeric 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 polyamides or polyesters, is the easier synthesis of polyolefins with polar comonomers [52, 53]. Polar monomers incorporated can contain hydroxyl, carboxyl, ether, ester, siloxy, or amino groups. In this work could be shown that it is possible to copolymerize different vinyl ethers such as allyl ethyl or propyl ether, hexenyl or decenyl butyl ether, and octadienylmethyl ether with ethene. The incorporation of the comonomer into the polymer chain depends on the polymerization temperature, the comonomer concentration and the used metallocene complex. Blends containing small amounts of such functional metallocene based copolymers are tougher and stiffer than not compatibilized polymers [54, 55].

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

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