Rend. Fis. Acc. Lincei (2017) 28 (Suppl 1):S87–S95
DOI 10.1007/s12210-016-0588-5

The discovery and evolution of metallocene-based olefin polymerization catalysts

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Received: 6 July 2016 / Accepted: 27 November 2016 / Published online: 15 December 2016

Abstract The development of the homogeneous metallocene/methylaluminoxane catalyst for the polymerization of olefin has widely increased the possibilities in controlling the polymer composition, polymer structure, tacticity and special properties with high precision compared to the heterogeneous Ziegler–Natta and Phillips catalysts. Metallocene catalysts allow the synthesis of isotactic, isoblock, syndiotactic, stereoblock or atactic polymers, as well as polyolefin composite materials with superior properties and low content of extractables. The homogeneous character of metallocene-based catalysts leads to a better understanding of the mechanism of the olefin polymerization and allows the synthesis of optically active olefin oligomers using chiral transition metal complexes. These 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. Such copolymers are suitable for blends of polyolefins with polyethers and other polar polymers because of an excellent adhesion of the two polymers. In the future, polyolefin nanocomposites and tailored copolymers open up the approach to new classes of materials with great property combinations such as improved stiffness, high gas barrier properties, significant flame retardancy, and high crystallization rates.

Keywords Metallocene · Catalysts · Methylaluminoxane · Polyolefin · Nanocomposites

1 Introduction

Polyolefin prepared by transition-metallic catalysts has grown to the largest industrial application for polymers. Today, about 150 million tons of polyolefin—the half of all plastics production—are produced worldwide per year, the majority with the help of heterogeneous Ziegler–Natta and Phillips catalysts (PlasticsEurope 2015). More than 50 years after the Nobel Prize was awarded to Karl Ziegler and Giulio Natta in 1963 the catalytic polymerization of olefins has not lost its fascination. Polyolefin is not only the polymer with the highest production volume, but it shows an unbroken production increase. Containing only carbon and hydrogen atoms, polyolefin is a sustainable material, light in weight and with a wide variety of properties.

A new development in this research field was the discovery of metallocene and other transition metal complexes activated by methylaluminoxane (MAO). 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 conditions. In addition, their catalytic activity is about 100 times higher than the

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This contribution is the written, peer-reviewed version of a paper presented by a participant to the Conference “Concepts in catalysis: from heterogeneous to homogeneous and enzymatic catalysis” held at Accademia Nazionale dei Lincei in Rome on February 25–26, 2016.

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classical Ziegler–Natta systems and can produce 40 million g of polyethylene by 1 g of metallocene. The metallocene/MAO catalysts were discovered at the Institute of Technical and Macromolecular Chemistry at the University of Hamburg (Kaminsky 2012). MAO plays an important role in the polymerization activity. It was found, that MAO is a mixture of different oligomers, including some ring structures (Fig. 1).

Even today the exact structure is not known, because there are equilibria with the oligomers, complexation of the oligomers towards each other and with unreacted trimethyl aluminum (TMA). MAO is a compound in which aluminum and oxygen atoms are arranged alternately and free valences are saturated by methyl substituents (Sinn et al. 1995).

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.

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 (Eq. 1).

$$\mathrm{Cp_2Zr(CH_3)Cl} + \mathrm{MAO} \rightarrow [\mathrm{Cp_2Zr(CH_3)}]^{+} + [\mathrm{MAO\text{-}Cl}]^{-} \tag{1}$$

Essential to the polymerization activity would be the formation of bulky anions with a week bonding to the metallocene cations. Knowing that the bulky structure of MAO could be necessary for the activation of metallocene catalysts, other bulky and weakly coordinating co-catalysts such as tris(pentafluorophenyl)borane or organic salts of the tetrakis(pentafluorophenyl)borate $[(C_6F_5)_4B]^-$, and aluminum fluorides were introduced (Bochmann 2010).

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

2 Homo-polyolefins

Metallocenes, especially zirconocenes but also titanocenes, hafnocenes1, and other transition metal complexes, combined with MAO, 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 (Scheirs and Kaminsky 2000; Coates 2000; Rieger et al. 2003; Kaminsky and Luinstra 2010; Nomura and Liu 2011; Kaminsky 2013; Delferro and Marks 2011). The homogeneous catalyst Cp_2ZrCl_2/MAO, produce polyethylene (PE) with a high activity of 60,000 kg PE/mol_{Zr} h, a molecular weight of 620,000 g/mol, 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. The homogeneous character of metallocene-based catalysts leads to a better understanding of the mechanism of the olefin polymerization and allows the precise polymer structure and composition in copolymers. Some selected zirconocenes with different symmetries and substitutions are shown in Fig. 2. There is a great variety of the structure of metallocenes, which can be used for the polymerization. Such and similar metallocenes are used for the polymerization of ethene, propene, and other olefins.

Generally zirconium catalysts are more active than hafnium or titanium systems. Titanium catalysts easier reduce to titanium-III complexes, which are catalytically inactive. Hafnium catalysts are generally slower. 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 amido-fluorenyl ligands. 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 (Kawai and Fujita 2009).

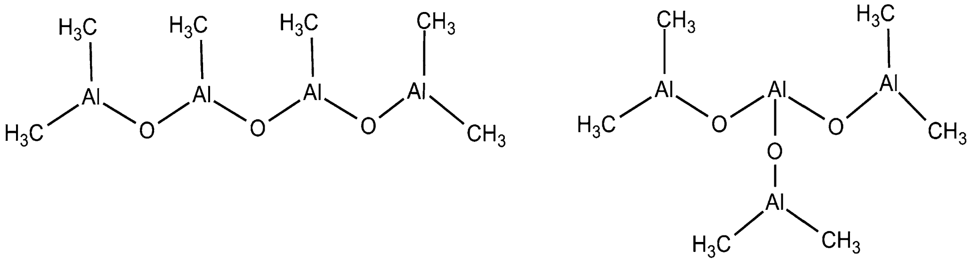
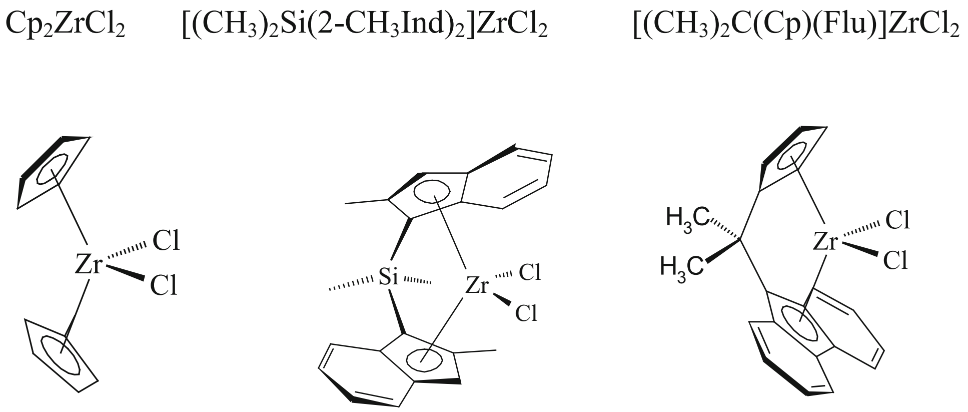


Fig. 1 Unit structures of methylaluminoxane (MAO)

Fig. 2 Selected metallocenes for the polymerization of olefins



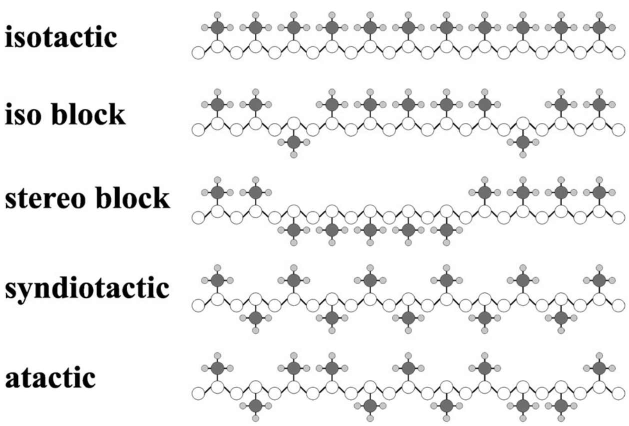


Fig. 3 Microstructures of polypropylenes obtained by various metallocene catalysts (hydrogen atoms of the backbone chain are not shown)

For an industrial use it is be necessary to support the MAO co-catalyst 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) (Hlatky 2000). By this procedure, a better particle morphology control is possible and there is less reactor walling.

Using metallocene/MAO catalysts it is possible to produce different kinds of microstructures such as isotactic, isoblock, stereoblock, syndiotactic, and atactic polypropylenes in high purity (Fig. 3). It was shown in 1984 that with chiral *ansa* metallocenes, in which the cyclic ligands are bridged and by this stabilized in the steric form, first isolated by Brintzinger (Wild et al. 1982), in combination with MAO a highly isotactic polypropylene (Kaminsky et al. 1985) was produced.

In 1987 pure syndiotactic polypropylene was obtained using a c_s-symmetric [$Me_2C(Flu)(Cp)]ZrCl_2$ complex (see Fig. 2) with a bridged cyclopentadienyl and a fluorenyl ring (Ewen et al. 1988; Razavi 2013).

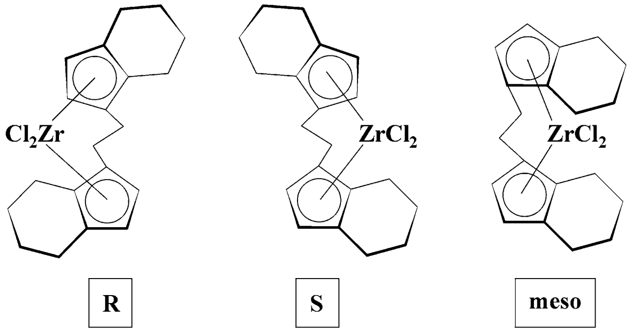


Fig. 4 Structures of the *R*, *S*, and *meso* form of $[En(ThInd)_2]ZrCl_2$

The activities vary between 130 and 15,000 kg PP/mol_{Zr} h at 30 °C and the molecular weights between 2000 and 750,000 g/mol. A high isotacticity of 98% was obtained using $[(CH_3)_2Si(2\text{-}CH_3Ind)_2]ZrCl_2$ as catalyst component. Non-chiral *ansa* metallocenes such as Cp_2ZrCl_2 (Fig. 2) produce atactic polypropylene.

The homogeneous chiral metallocene catalyst systems offer another possibility. The synthesized $[En(ThInd)_2]ZrCl_2$ is a mixture of the *R* and *S* form; UV-light changes the compound into the *meso* form (Fig. 4). By insertion of propene or higher 1-olefins, a new stereo center is formed in the growing polymer chain. In heterogeneous Ziegler–Natta catalysts the amount of stereospecific centers with *R*- and *S*-configuration is equal, thus inserting propene in the Fischer projection in the same quantity with the methyl group to the top and to the bottom.

The insertion should give only one configuration by using only one ansa zirconocene enantiomer. Hans-Herbert Brintzinger succeeded in separating *R*- and *S*-ansa zirconocene complexes by preparation of diastereomers with optically active compounds like (*R*) binaphthol or *O*-acetyl-(*R*)-mandelate (Schäfer et al. 1987). We used the mandelate complex since its catalytic activity is similar to that of the corresponding dichloride and it can be obtained in high purity (Fig. 5) (Kaminsky et al. 1989).

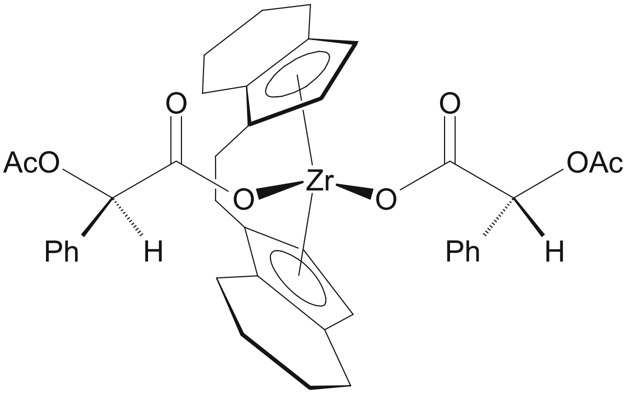


Fig. 5 Structure of (*S*)-[1,1′-ethylidene-bis(4,5,6,7-tetrahydro-1-indenyl)]zirconiumbis(*o*-acetyl-(*R*)-mandelate and methylaluminoxane

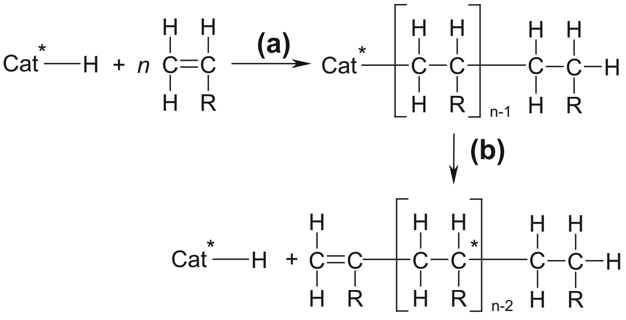


Fig. 6 Reaction scheme for the oligomerization of olefins by chiral zirconocene/MAO catalysts: *a* initiation and propagation, *b* chain termination

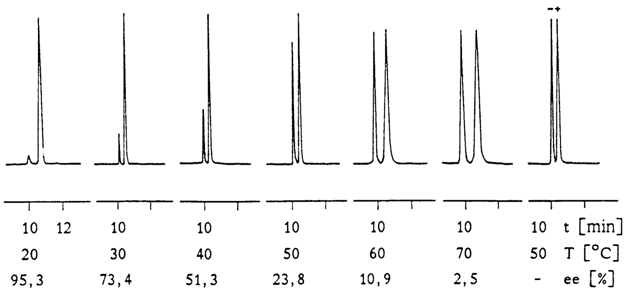


Fig. 7 Asymmetric oligomerization of propene; gas chromatographic separation of 2,4-dimethyl-2-heptene (trimer) using a octakis(6-*o*-methyl-2,3-di-*o*-pentyl)cyclodextrin phase

Only the *S*-ansa zirconocene forms a complex while the *R*-form does not react with the *R*-mandelate. The complex was separated by crystallization from the unreacted form and obtained in a purity of 99%. The polymerization starts when an olefin undergoes insertion into the zirconium carbon bond formed by methylation with MAO.

Subsequent insertions lead to oligomer or long alkyl chains (Fig. 6a) and chain growth termination takes place by hydrogen transfer to the transition metal center or a metal-bound olefin, resulting in formation of a zirconocene hybrid or alkyl and an olefin terminated polymer or oligomer chain (Fig. 6b). The trimeric oligopropene has one chiral carbon, the tetrameric two. To receive oligomers a high *S*-zirconocene and a very low propene concentration is needed. Propene was fed continually for this oligomerization at different reaction temperatures. The yield of trimers was up to 14%. They were separated by distillation from the other oligomers. But also the trimers were a mixture of different isomers. At 20 °C oligomerization temperature and a propene feed of 10 ml/min 90% of the trimeric fraction consists of 2,4-dimethyl-1-heptene. Other isomers were formed by double bond migration, 2,1- and 1,3-insertion and were a first evidence for the mechanism of chain termination in the olefin polymerization by metallocene catalysts.

The trimeric 2,4-dimethyl-1-heptene could be separated by gas chromatographic separation of racemic mixtures into the pure enantiomers by a cyclodextrin phase (Fig. 7).

It can be seen that a trimer with 95.3 enantiomeric excess (ee) was obtained at 20 °C oligomerization temperature. The tetrameric oligopropylene shows a higher optical rotation than the trimeric. This was the direct proof that a chiral (pure enantiomer) homogeneous metallocene/MAO catalyst produces optically active oligomers and isotactic polymers. Similar results had been found by Pino (Pino et al. 1987) using hydrooligomerization to obtain saturated branched alkanes.

3 Copolymers

Metallocene/MAO catalysts are not only suitable for the homopolymerization of ethene and propene, but also for copolymerization with different comonomers (Stadler et al. 2011). 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, ethene propene diene monomers (EPDM), linear low density polyethylene (LLDPE) are of high interest for polymer industries. Most production plants built today for EP and EPDM use metallocene catalysts.

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 (Frediani et al. 2006) or with ethene/propene oligomers in two steps. In the last case, polymers with crystalline polyethylene backbone chains and amorphic ethene/propene copolymer side chains are obtained.

Figure 8 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 8000 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-di-*tert*-Bu_2Flu)(Cp)]$ZrCl_2$ was used to catalyze the copolymerization (Step B).

The copolymerization of cyclic olefins such as cyclopentene or norbornene with ethene and other α-olefins results in cycloolefin copolymers (COC), representing a new class of thermoplastic, amorphous materials (Kaminsky et al. 2012; Boggioni and Tritto 2014). 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.

Most metallocenes produce polymers with a statistical structure, few others 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. Meanwhile, ethene–norbornene COC materials are commercially produced.

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 (Säppälä et al. 2013). It is one way to modify the properties of a polymer, because these functional groups control important polymer

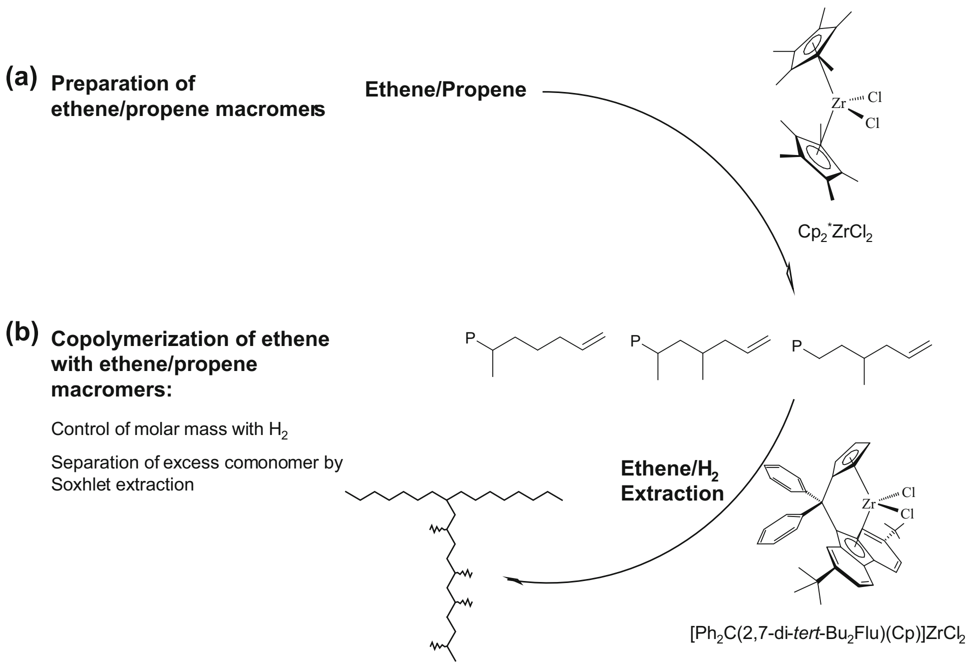


Fig. 8 Reaction scheme for ethene-*graft* ethene/propene copolymers by two different zirconocene/MAO catalysts in two steps

properties such as adhesion, barrier and surface properties, solvent resistance, miscibility with other polymers, and rheological properties. The functionalization of polyolefin offers a possibility to broad applications in areas, less explored before. Only few functionalization processes are available and the obtained copolymers do not have 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 (Kaminsky and Fernandez 2008). 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 are used: allyl ethyl ether (AEE), allyl propyl ether (APE), 5-hexenyl butyl ether (HBE) (Kaminsky and Fernandez 2015).

Figure 9 shows the dependence of the incorporation rate of the ether with redundancy of the 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. A maximum of the incorporation rate for AEE is observed at an ether concentration of 0.04 mol/L.

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 6500 for APP. The decrease of the activity with the ether concentration in the feed was higher for APE than that for AEE.

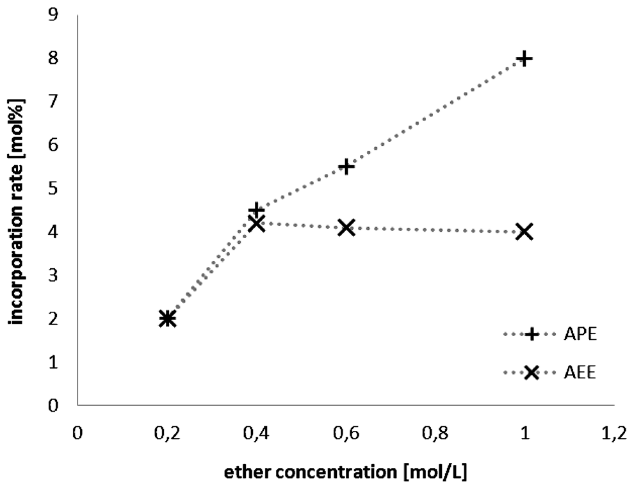


Fig. 9 AEE and APE incorporation (wt%) into the copolymer in dependence of the ether concentration in the feed

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 activities are very high for low ether concentration (79,300 kg copolymer/mol zirconocene in 1 h) in the starting phase, but decreases hardly if the concentration decreases although the polar monomer was treated with triisobutyl aluminum (TIBA) as an complexation agent

4 Polyolefin nanocomposites

Polyolefin nanocomposites are of great interest because of their high potential as materials with novel properties (McNally and Poetschke 2011). 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 (Kaminsky 2014). 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 (Fig. 10). 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 multi-walled carbon nanotubes (MWCNT) are an especially attractive class of fillers for polymers because of their intriguing mechanical and thermal properties (Kaminsky et al. 2008).

The fiber/MAO/zirconocene system worked like a supported catalyst. The polymerization activity reached 5000 kg PP/mol Zr h [propene]. It was independent of the

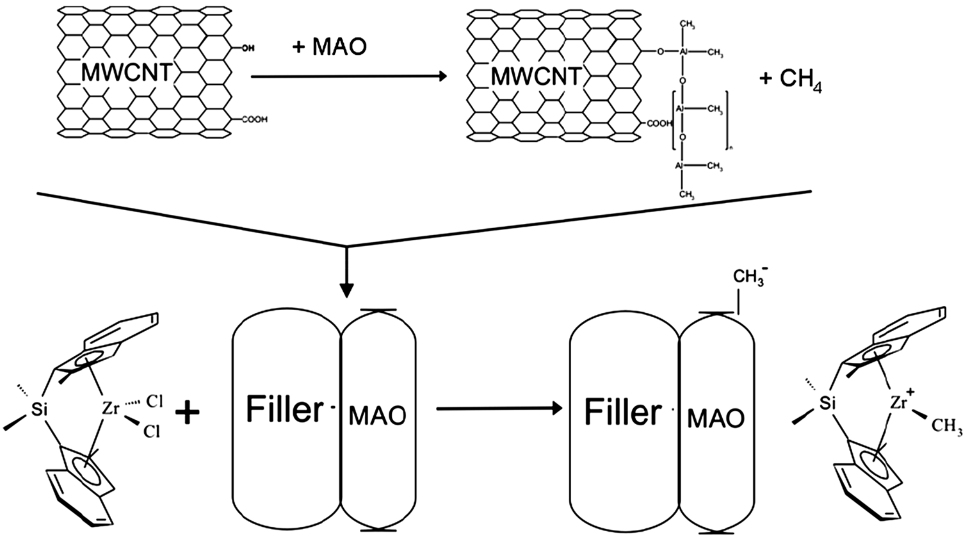


Fig. 10 Formation of activity sites: absorption of MAO on oxidized multiwall carbon nanotubes (MWCNT) followed by addition of a zirconocene

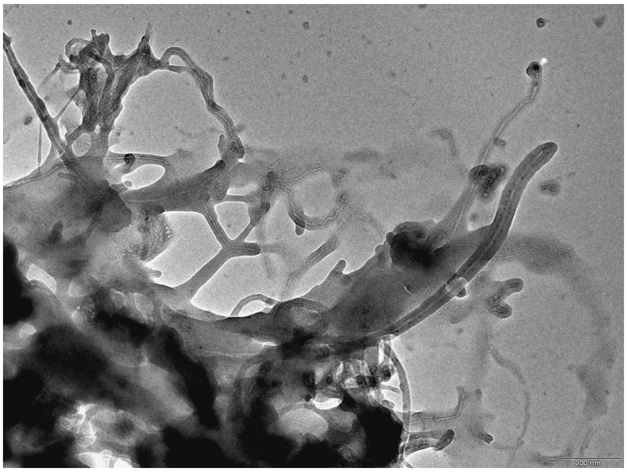


Fig. 11 TEM micrographs of a MWCNT composite prepared by in situ polymerization covered by iPP

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. 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 Fig. 11 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. Even the loose network of polymer-layered nanotubes on the lower left side, which are partially conglomerated 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 increase strongly and make this composite material suitable for new applications such as in the automotive plastic industries (Lozano et al. 2001). The form stability temperature increases from 48.7 °C for pure iPP to 71.5 °C for a composite iPP containing 2.3 wt% MWCNT.

5 Outlook

The development of metallocene/methylaluminoxane catalysts has 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. This development will continue. 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. By these and modern Ziegler–Natta catalysis it is possible in polyolefin research to produce:

- All kinds of homopolymerization.
- Co- and simple block copolymers.
- Tailored tacticities of the backbone chain.

- Polyolefin composites by co-extrusion and in situ polymerization.
- Organization of the backbone chain, e.g., by gel spinning.

In the future it will become possible to produce:

- Defined polyolefin copolymers with a tailored sequence.
- Defined combination of polar and unipolar monomers.
- Tailored three-dimensional polyolefin structures.
- Composite materials with organized nanoparticles.

The known dependence of metallocene-based polymers from the catalyst structure allows the modeling of their reaction kinetics and the polymerization process. 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 polyolefin with tailored molecular weight, comonomer content, long and short chain branching, 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 polyolefin 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 polyolefin with other polymers such as polyamides or polyesters, is the easier synthesis of polyolefin with polar comonomers. Polar monomers incorporated can contain hydroxyl, carboxyl, ether, ester, siloxy, or amino groups. Blends containing small amounts of such functional metallocene-based copolymers are tougher and stiffer.

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

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