

Development of *ansa*-Metallocene Catalysts for Isotactic Olefin Polymerization

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Abstract The development of *ansa*-metallocene catalysts is considered along several lines of interest – *ansa*-metallocene complexes with different ligand frameworks, insights gained with regard to relevant reaction intermediates and contributions of *ansa*-metallocene catalysts to industrial polymer production – with a view toward the present state of the art in these fields of catalysis research.

Keywords Activation · *ansa*-Zirconocene catalysts · Constrained-geometry catalysts · ethene/propene rubbers · Isotactic polypropylene · Linear low-density polyethylene · Molar-mass distribution · Olefin polymerization · Reaction mechanisms · Single-site catalysts · Stereoselectivity

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1 Introduction

In this article, we try to give a brief account of the development of *ansa*-metallocene catalysts for isotactic olefin polymerizations, especially with regard to some points of particular interest to the authors of this article. For this, we will refer to appropriate previous reviews and then try to assess the state of the art.

2 Structural Variants of *ansa*-Metallocene Catalysts

In the three decades that have passed since the first syntheses of chiral ethanediyl-bridged bis(indenyl)titanium and bis(indenyl)zirconium complexes [1, 2] and the first reports on their use – together with methylalumoxane as activator [3] – as catalysts for isotactic olefin polymerization [4, 5], this field of catalysis research has seen many structural variations on the *ansa*-metallocene theme.

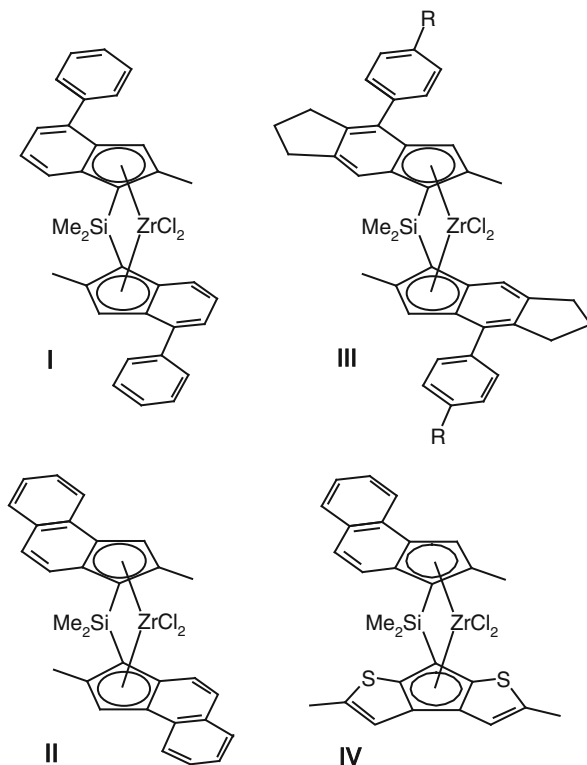
Among *ansa*-metallocene catalysts with different group IV transition metals, *ansa*-titanocene-based catalysts (with rare exceptions [6]) lose most of their activity above 0°C, whereas *ansa*-hafnocene catalysts usually give lower activities than the analogous *ansa*-zirconocene catalysts [7, 8], which have thus received most research interest.

Variations in catalyst structures mostly involved changes in the substitution patterns of the *ansa*-metallocene ring ligands, since catalyst properties are clearly influenced most directly by the steric environment of the metallocene coordination sites [7–9]. Much interest has been directed at the possibility of obtaining polyolefins with tacticities different from those of the isotactic polymers obtained with C₂-symmetric *ansa*-metallocene catalysts. The observation that zirconocene catalysts with C_S-symmetric geometry, i.e. with enantiotopic metallocene coordination sites, generate syndiotactic polypropylene [10] thus helped to establish explanations for the enantioselectivity of the chain-growth process; these explanations are universally accepted today [11, 12].

Especially interesting in this regard are *ansa*-metallocene catalysts with a C₁-symmetric structure, in which the steric environments of the metallocene coordination sites are unrelated to each other. Depending on the steric environment of each coordination site, polypropylene tacticities can range here from almost atactic to highly isotactic [7, 13]. Due to the possibility of finely adjusting stereoerror frequencies, and thereby tuning the flexibility of polymer chains and the ensuing properties of polymer materials, this type of catalysts continues to be of practical interest [14].

With regard to variations in bridging units, interanular bridging via a (CH₃)₂Si unit proved to endow *ansa*-metallocene catalysts with higher degrees of stereoselectivity and with higher activities than bridges with two-atom or longer chains [15], probably due to a greater stereoridity of the ligand framework and a wider opening of the interanular wedge angle [7, 8, 16]. Bridging units with spatially more demanding, asymmetric or chiral substituents have likewise been shown to influence the catalytic properties of *ansa*-metallocene catalysts [17], especially those with C₁ symmetry [7], presumably via their effects on ring-ligand conformation.

Fig. 1 Representative *ansa*-zirconocene precatalysts: After activation with MAO, **I** and **II** give highly active catalysts for isotactic propene polymerization [20, 21], **III** gives further activity increase [22] and C_1 -symmetric **IV** gives partly isotactic polypropylene [14]



Ansa-metallocene catalysts with ring ligands connected by a semi-labile electron donor–acceptor bond have been shown to produce polypropylene with interesting elasticity properties [18]. Similar observations had also previously been made with unbridged zirconocene catalysts, the indenyl ligands of which are hindered in their mutual rotation by phenyl substituents in their 2-position [19]. In both cases, an interchange between alternative ring ligand rotamers appears to occur on a time scale that is comparable to that required to complete a polyolefin chain. Whether this gives rise to polymer chains containing alternating blocks of preponderantly isotactic and atactic sequences as a cause of elastomeric properties, or to reactor blends of mainly isotactic and mainly atactic chains (or both), is still under debate [8].

Major research interests have been aimed at the adjustment of *ansa*-metallocene catalysts to the requirements of industrial polymer production, i.e. high activities, high molar masses and high degrees of isotacticity. Remarkable achievements in this regard by use of *ansa*-zirconocene complexes with methyl-substituted 2-positions and extended anulation and/or “frontal” substitution of their C_5 -ring ligands (Fig. 1) were reported rather early on [20, 21] and were further optimized more recently [22, 23].

A “frontal” extension of the ring ligands appears to be responsible for increased activities, most likely by way of destabilizing some (still unidentified) resting state of the chain-growth process. On the other hand, methyl substituents in the

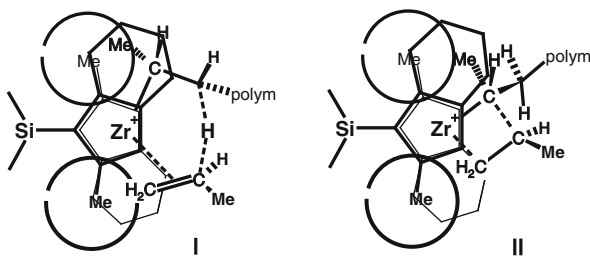


Fig. 2 The transition state for β -H transfer to monomer (**I**) after a 2,1-insertion requires more space in the mid-plane of the metallocene wedge than the insertion transition state (**II**); it is thus disfavored by methyl substituents next to the bridgehead positions [21, 24]

2-position, next to the interanular bridge, were shown to suppress chain release via β -H transfer to an olefin monomer, particularly after a 2,1-misinsertion, due to their interference with a space-demanding β -H transfer transition state (Fig. 2) [21, 24].

A more recent variation of this theme concerns the utilization of *ansa*-zirconocene catalysts of the bis-indenyl type for the industrial production of elastomeric propene/ethene copolymers (EP rubbers, see Sect. 4) [8]. Here, a drastic reduction in molar mass occurs in the presence of ethene. This problem was overcome by further decreasing the space in the *ansa*-metallocene coordination plane through replacement of one of the 2-positioned methyl substituents by an isopropyl group [25]. This feat represents a rare case where a prediction based on computational studies actually preceded the experimental outcome and shows the usefulness of clear conceptions concerning relevant reaction paths.

3 Mechanisms of Catalyst Activation and Polymerization Catalysis

The first reports of isotactic α -olefin polymerization by homogeneously dissolved *ansa*-metallocene catalysts were greeted by the expectation that the mechanisms responsible for this stereoselective catalysis might now be more thoroughly clarified than had been possible for solid-state Ziegler–Natta catalysis. Although progress has been made toward that goal during recent decades, our basic understanding of homogeneous polymerization catalysis is still not quite satisfactory in some respects.

Activation of *ansa*-metallocene dichloride precursors by methylalumoxane (MAO) – a partial-hydrolysis product of trimethylaluminum [3] – was the initial door-opener for the polymerization of propene and higher olefins by *ansa*-metallocene catalysts [4, 5]. It is still being quoted as the most frequently used route to activate these catalyst systems [26]. Evidence has recently been presented that activation by MAO might involve highly reactive AlMe_2^+ cations [27]. Yet it remains unknown which structural features of MAO might be responsible for its unique reactivity.

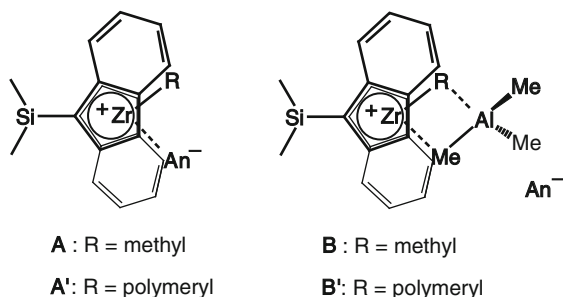


Fig. 3 Inner-sphere ion pairs **A**, containing a methyl zirconocenium cation, and outer-sphere ion pairs **B**, containing a heterobinuclear AlMe₃ adduct of the latter, together with a weakly coordinating anion An⁻, such as MeB(C₆F₅)₃⁻, B(C₆F₅)₄⁻ or MeMAO⁻, observed in *ansa*-zirconocene systems activated with B(C₆F₅)₃, Ph₃CB(C₆F₅)₄ or MAO, respectively [26, 28, 29]. The corresponding species **A'** and **B'** with R = polymeryl, observed in active catalyst systems in the presence of olefin [30, 31]

Highly active and more well-defined catalyst systems have become accessible by reaction of a zirconocene alkyl precursor with one of several “cationization” reagents that contain a trityl or dimethylanilinium cation capable of abstracting an alkyl anion from this precursor. An inert tetra(perfluorophenyl) borate or related anion coordinates only weakly to the resulting alkyl zirconocenium cation in an inner-sphere ion pair of type **A** (Fig. 3) [26, 28, 29].

In MAO-activated catalyst systems, alkyl zirconocenium cations are likewise thought to be present, presumably in weakly bound inner-sphere ion pairs with anions of the type MeMAO⁻ [26, 29]. These anions – still only vaguely characterized as large agglomerates [32] – are assumed to be formed from MAO by uptake of a methyl anion from the alkyl zirconocene precursor. In equilibrium with these inner-sphere ion pairs **A**, outer-sphere ion pairs **B** (Fig. 3) are observed in MAO-activated pre-catalyst systems [29, 32–34] that contain a heterobinuclear cationic AlMe₃ adduct [35], presumably together with MeMAO⁻ as counter-anion.

With regard to the growth of metal-bound polymer chains from a metallocene pre-catalyst activated in this manner, it is undisputed that successive monomer molecules are incorporated by *cis*-insertions into the metal–alkyl bond, first of an ion pair **A**, and then of the ensuing metal–polymeryl species **A'** [7]. The latter reaction, i.e. growth of a Zr-bound polymer chain, has been found to be much faster than the initial insertion into a Zr–Me bond in most cases studied [30, 36, 37].

For the growth of isotactic polypropylene chains and higher polyolefin chains at the chiral coordination sites of *ansa*-metallocene catalysts, the following explanation is now firmly established [11, 12]: Formation of the new C–C bond requires that the α -olefin substituent and the C(α)–C(β) bond of the metal-bound polymeryl chain are oriented *anti* to each other along the incipient C–C bond, while the C(α)–C(β) chain segment must reside in an open quadrant of the chiral metallocene coordination site. The latter is thus considered to control the enantiofacial orientation of the α -olefin in the insertion transition state **TS** (Fig. 4) by way of the C(α)–C(β) chain-segment “lever”.

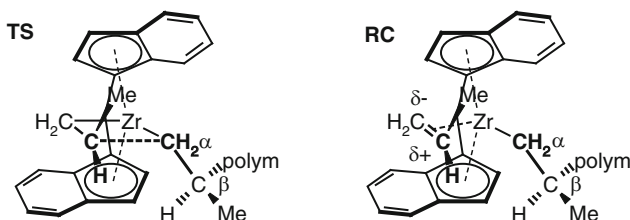


Fig. 4 Transition state **TS** for favored si-facial olefin insertion into a Zr–polymeryl bond according to the model of chain-segment-mediated catalytic site control [11, 12] (left) and reaction complex **RC**, which is thought to precede transition state formation [7] (right)

This model of chain-segment mediated enantiomorphic site control for isotactic polyolefin formation by C_2 -symmetric *ansa*-metallocene catalysts has received experimental support from several lines of stereochemical evidence [38, 39]. It has also provided convincing explanations for the generation of syndiotactic polypropylene at the enantiotopic coordination sites of C_S -symmetric *ansa*-metallocene catalysts [10] and for the variable stereoregularities of polymers obtained with C_1 -symmetric catalysts cf. Sect. 2) [7, 13].

Useful insights regarding the transition states of side reactions, which occur in competition to olefin insertion, such as chain release by β -H transfer and chain-end isomerizations, have also been derived from experimental data on kinetics [21, 40, 41], kinetic isotope effects and isotope label redistributions [39, 42].

Little experimental evidence is available, on the other hand, with regard to a metal-olefin reaction complex **RC** (Fig. 4), which is considered to precede formation of the insertion transition state **TS**. Steady-state concentrations of such a species are obviously insufficient for spectroscopic detection. Experimental studies on cationic metallocene–olefin complexes, where olefin insertion is slow or impossible for one reason or another, as well as a number of computational studies, portray such reaction complexes as having some finite stability, a rather polarized C=C double bond and a low barrier of rotation around the olefin–metal bond [7, 28].

Insufficiently explored is also the ubiquitous reaction by which a metallocene-bound polymer chain is transferred to an Al center of the co-catalyst/activator in exchange for a methyl group. While there is little doubt that intermediates of type **B'** (Fig. 3) are involved in such an alkyl exchange [28], only scant experimental data concern the effects of different chain-ends and *ansa*-metallocene structures on the rate, extent and direction of these exchange reactions. As these can be used to transfer polymer chains between catalysts with different stereoselectivities [43], further exploration might be useful for a production of polypropylene that contains chain segments with different tacticities.

Rather glaring deficits in our understanding of metallocene-catalyzed olefin polymerization concern the catalyst resting state(s), i.e. the identity of those species that make up the majority of the total metallocene concentration of a catalyst system “at work.” At first glance, it would appear quite feasible to identify at

least the major species of such a working catalyst, e.g. by NMR spectroscopy. In this manner, inner-sphere ion pairs of type **A'** (Fig. 3), with a polymeryl chain and a $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ anion attached to the cationic metal center, have indeed been identified in toluene solution at -40°C as the catalyst resting state in an *ansa*-zirconocene catalyst system activated with the Lewis-acidic borane $\text{B}(\text{C}_6\text{F}_5)_3$ [30].

Under conditions more closely approaching practically useful polymerization catalysis, i.e. in working catalyst systems that contain less “sticky” counter-anions and a substantial olefin excess and that operate at ambient or higher temperatures, it is not yet clear which fractions of the total catalyst content in a given catalyst system correspond to ion pairs of type **A'** or to several other resting-state candidates with regio-irregular [44], allylic [45] or agostically bound [46] chain ends.

During polymerization of 1-hexene by an MAO-activated *ansa*-zirconocene catalyst system, species of types **A**, **B** and **B'** were detected by NMR spectroscopy but found to account for less than half of the initial metallocene concentration [31]. Major parts of the metallocene content of this catalyst system thus remain unaccounted for.

Further efforts to identify the resting state(s) and the major modes of deactivation [47] of typical *ansa*-metallocene catalysts would appear worthwhile, since – to quote a recent review [26] – “in the absence of this information, a rational analysis of the effects of structural variations on catalyst activities ... must remain fragmentary.”

4 Industrial Use of *ansa*-Metallocene Catalysts

The first isospecific propene polymerization with an ethanediyl-bridged bis(indenyl)-titanium complex demonstrated in 1983 the capability of *ansa*-metallocenes to control the tacticity of a growing polypropylene chain [4, 48], thus creating a strong interest in exploring the potential use of *ansa*-metallocenes for industrial polypropylene production. A first step towards industrially suitable systems was the use of much more stable zirconium complexes, which when activated by the methylaluminoxane co-catalyst [3] allowed higher polymerization temperatures and thus higher activities [5].

However, these first *ansa*-zirconocenes delivered at temperatures of 70°C and above, as typical for industrial PP processes, only oligomeric or low molecular weight polypropylene and moderate isotacticities, both still insufficient for industrial usage. Further increases in activity and better stereospecificities were obtained using the more rigid dimethylsilylene bridge, which was patented by Fina Technology in 1987 [15, 49] and has since become the most widely used bridging unit.

However, only the introduction of methyl substituents in the 2-position, by the former Hoechst AG in 1990 [20, 50], led to polypropylenes with sufficiently high molar mass under industrially relevant polymerization conditions. In 1990, *rac*-dimethylsilylene-bis(2-methylindenyl)zirconium dichloride thus became the first *ansa*-metallocene to combine all these improvements and be suitable for industrial use [50, 51]. Since then, the basic concept of dimethylsilylene-bridged,

2-methyl-substituted bisindenyl zirconocenes has been further optimized, e.g. by substitution at the 4-position [52–54] and by pseudo C_2 -symmetric bisindenyl *ansa*-zirconocenes with one 2-isopropyl and one 2-methyl substituent [25, 55].

Probably to circumvent the former Hoechst AG's strong patent position on bisindenyl-type *ansa*-metallocenes, alternative structures were developed by Mitsubishi Chemical Corporation [23, 52] and by former Montell [14, 56], based on azulenyl and heterocenyl ligands, respectively.

Although *ansa*-metallocene catalysts are intrinsically homogeneous catalysts, all industrial polypropylene processes had been developed for heterogeneous Ziegler–Natta catalysts. Therefore, an absolute requirement for the industrial use of *ansa*-metallocenes was their heterogenization on a solid carrier material to avoid polymer growth on reactor walls and to achieve control over polymer particle morphology [57, 58]. Fixation of an *ansa*-metallocene catalyst on a solid support allows its use as a “drop-in” replacement for traditional Ziegler–Natta solid-state catalysts in preexisting polyolefin production plants, where it then produces polyolefin materials with properties closely similar to those produced by it in homogeneous solution. The necessity to heterogenize metallocene catalysts was first recognized by ExxonMobil and patented in 1985 [59]. Since then, suitable recipes for heterogenized metallocene catalysts, which yield polymer products with controlled spherical morphology, and the elementary processes responsible for this outcome have been thoroughly researched and described in detailed reviews [57, 58, 60, 61].

Industrial use of *ansa*-metallocenes for the production of isotactic polypropylene had to overcome not only technical hurdles, but has also been restricted by a complicated and scattered patent landscape. Basic patent rights like the activation of metallocene complexes by MAO, supported metallocenes [59, 62], silanediyl-bridges [49] and 2-methyl substitution [50], all of which were required for the use of *ansa*-metallocenes in industrial polypropylene production, were owned by different companies such that no player had the freedom to move. Only in 1995, 5 years after *rac*-dimethylsilylenbis(2-methylindenyl)zirconium dichloride had been described for the first time in a patent [50], did ExxonMobil and the former Hoechst AG announce independently their first commercial production of metallocene-catalyzed, isotactic polypropylene. Most likely, these 5 years were needed not only to solve technical problems, but also to gain access to all the necessary patent rights.

Today, at least five companies are known to use *ansa*-metallocenes for industrial production of isotactic polypropylene: TOTAL Petrochemicals & Refining (Lumicene[®]) [63], LyondellBasell (Metocene) [64], Japan Polypropylene (WINTEC[™]), ExxonMobil (Achieve[™] PP) and LyondellBasell's licensee PolyMirae (Metocene). In addition, technology for the industrial production of polypropylene by use of *ansa*-metallocenes is offered for licensing by LyondellBasell (Metocene) [64] and Lummus Novolen Technology GmbH (Novocene[™]) [65]. Although Japan Polypropylene's WINTEC[™] is produced by a bis-azulenyl-type *ansa*-metallocene [23, 52] and also uses a MAO-free activator support, all others are believed to use bis-indenyl-type metallocenes.

In industrial use, *ansa*-metallocene catalyst systems compete with the well-established traditional Ziegler–Natta catalysts. Because their precursors, in particular the racemic *ansa*-metallocenes and suitable activators like MAO, are more costly than the relatively simple raw materials for Ziegler–Natta catalysts, the industrial success of *ansa*-metallocene catalysts is contingent on their ability to produce polymer materials with superior properties, which can be priced so as to compensate for the higher costs of synthesizing, activating and handling these advanced organometallic catalysts.

For isotactic polypropylene (i-PP), currently produced at a world-wide scale of about 50 million tons per year with classical Ziegler–Natta catalysts, the situation can be viewed as follows [66]: For many applications, the rather wide molar-mass distribution of i-PP generated by solid-state Ziegler–Natta catalysts is an advantage compared to the narrow molar-mass distribution of i-PP produced with supported *ansa*-metallocene catalysts, since a wide molar-mass distribution leads to a more pronounced shear-induced viscosity decrease of the polymer melt and, hence, to higher through-put rates in typical extrusion processes. It also provides higher polymer-melt strengths, which is desirable in thermoforming and biaxially oriented polypropylene (BOPP) film production, both very large application segments for i-PP. Other i-PP applications (e.g. melt-blown or spun-bonded non-woven fabrics), however, benefit from metallocene-produced i-PP because they run more stably at higher speeds in these spinning processes, thus providing processing advantages. The uniform polymer chain lengths also cause a higher orientation in the spinning process, thus providing higher tenacities of the final non-woven fabric [67].

Besides its narrow molar-mass distribution, metallocene-produced i-PP benefits from a much more efficient control of its molar mass by hydrogen, eliminating the need for post-reactor chain degradation using peroxides. Metallocene-produced i-PP is thus normally free of oligomeric chain fragments and low molecular weight residues from peroxides, which both cause spinning fumes and deposits on the spinning dies. This reduces emissions during the spinning process and the frequency of shutdowns necessary to clean the spinning dies.

Although the wider molar-mass distribution of conventional i-PP is generally preferred in thick-wall injection molding, where the shear-induced drop of the melt viscosity helps to fill the mold faster, *ansa*-metallocene-catalyzed i-PP offers advantages in thin-wall injection molding, where i-PP with higher melt flow rate (lower viscosity) is generally used: The uniform polymer chain length distribution brings a higher number of tie-molecules capable of connecting different crystallites. This translates into higher toughness, whereas the absence of excessively long polymer chains (with very long relaxation times) reduces warpage and gives injection-molded articles higher dimensional stability and superior mechanical strength; consequently, thinner walls allow material savings.

Other advantages of these materials result from their crystallization characteristics: Due to its compositional homogeneity, polypropylene obtained with *ansa*-metallocene catalysts gives rise to a more controlled initial crystallite formation in a narrow temperature window. The ensuing crystallization process can thus be guided so as to yield smaller crystallites than in polymers obtained with

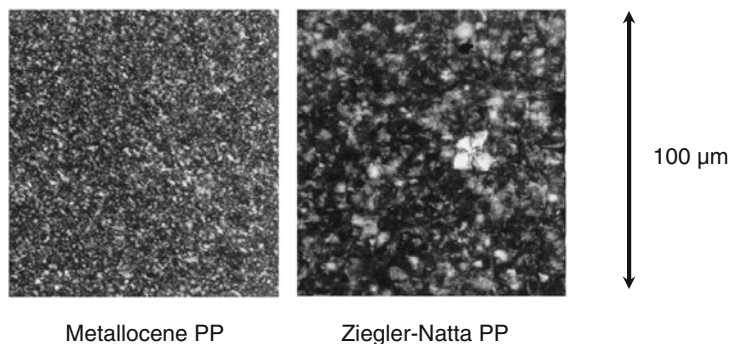


Fig. 5 Crystallite sizes in polypropylenes produced with an *ansa*-zirconocene catalyst (*left*) and with a solid-state Ziegler–Natta catalyst (*right*), both clarified with a nucleating agent (Courtesy of Basell Polyolefins GmbH and of Rendiconti Lincei: Scienze Fisiche e Naturali for permission to reproduce this figure from [66])

classical solid-state catalysts (Fig. 5). Therefore, films and thin-walled articles made from these materials have substantially reduced haze and close-to-perfect transparency, together with a decreased permeability for oxygen and water.

Ansa-metallocene catalysts, and metallocene catalysts in general, deliver particularly clear-cut improvements in product properties of ethene/ α -olefin copolymers [68], such as linear low-density polyethylene (LLDPE) or ethene/propene (EP) rubbers, which command large polymer market segments. Solid-state Ziegler–Natta catalysts, which strongly prefer ethene, need a large excess of α -olefin in the monomer feed to incorporate sufficient co-monomer fractions. Higher α -olefin contents are mostly built into short polymer chains, which grow at less-selective centers of these non-uniform catalysts. The resulting copolymers thus usually contain significant fractions of soft, short-chain materials, which are extracted from the surface of packaging films upon contact with lipids or cause other undesirable effects.

Metallocene-based single-site catalysts, on the other hand, incorporate propene and higher α -olefins more readily, easily generating copolymer chains with much higher co-monomer contents, controlled co-monomer distribution along the chains and uniform chain lengths [7, 8]. Their selectivities with regard to co-monomer uptake and co-monomer distribution within chains – from alternating to random or even blocky microstructures – can be tuned almost without limitations so as to allow access to copolymer materials with high suitability for various form-giving processes and with mechanical and optical properties widely adaptable to various end-user demands [8, 69]. In particular, films produced from metallocene-catalyzed LLDPE (m-LLDPE) show drastically improved mechanical strength, gloss and transparency compared with films of LLDPE obtained from conventional Ziegler–Natta catalysts. Therefore, Single-site catalysts, including metallocene and *ansa*-metallocene catalysts, are widely used for the production of ethene/ α -olefin copolymers and, in particular, m-LLDPE.

A majority of all polyethylene grades are ethene/ α -olefin copolymers (LLDPE, MDPE), which benefit directly from the use of single-site catalysts like *ansa*-metallocenes. Most polypropylenes, on the other hand, are homo-polymers, with one exception: biphasic i-PP reactor blends contain elastomeric ethene/propene copolymers (EP rubbers) dispersed in a matrix of crystalline i-PP homo-polymer. Such reactor blends, used e.g. in the manufacture of automobile parts, retain the high mechanical strength of isotactic polypropylene while being endowed with increased toughness, also at lower temperatures, from the dispersed EP rubber particles. However, these ethene/propene copolymers, for which similar considerations should hold as for m-LLDPE, were not accessible by first-generation 2-methyl-substituted bisindenyl *ansa*-metallocenes because of a drastic reduction in polymer chain length in the presence of ethene. Therefore, the development of catalysts bearing a ligand framework with suitably substituted α -positions [25, 55, 70], as discussed in Sect. 2, was a prerequisite for the production of i-PP reactor blends with metallocene catalysts. Such a specially adapted *ansa*-zirconocene catalyst is used by LyondellBasell to produce EP/i-PP “impact” polymer blends, which belong to their family of “Clyrell” grades [71].

The unique properties of i-PP produced with *ansa*-metallocene catalysts, including their low content of easily migrating short-chain polymer, desirable in particular for food and medical packaging and related purposes [72], has driven the industrial use of i-PP produced with *ansa*-metallocene catalysts in some demanding market sectors. However, higher costs, the dominance of homo-polypropylene, improved Ziegler–Natta catalysts and, last but not least, a complicated patent situation have as of today restricted their use in the i-PP field to specialized niche applications.

The possibility of controlling the interanular wedge angle of *ansa*-metallocene catalysts and their resulting capability to also enchain olefins, which are otherwise not readily amenable to insertion polymerization, allows the production of copolymers of ethene with cyclic olefins, in particular with norbornene or its substituted derivatives. Based on first observations in this regard [73, 74], ethene/norbornene copolymers, e.g. with alternating microstructures [75–77] and with excellent optical and barrier properties, are now commercially produced with *ansa*-metallocene catalysts by Topas Advanced Polymers (TOPAS[®]) [78] and by Mitsui Chemical (Apel) [79].

5 Concluding Remarks

Since the first reports on their usage for isospecific propene polymerization [4, 5, 48], *ansa*-metallocenes have inspired industrial and academic research for almost 30 years. Initially introduced for isospecific olefin polymerization, the concept of bridging their two ring ligands has substantially enhanced the variability and design options of metallocene catalysts in general. In addition to paving the way for industrial i-PP

production with single-site catalysts, this concept has also led to the first industrial production and market introduction of syndiotactic polypropylene by former Fina Inc. (today TOTAL Petrochemicals & Refining USA, Inc.) and of ethene/norbornene copolymers by former Hoechst AG (today TOPAS Advanced Polymers).

The possibility of preventing the mutual rotation of the ring ligands [4, 5] and to vary the interanular wedge angle [16] has secured for *ansa*-metallocenes an important role in metallocene-produced polyethylene, together with simple unbridged metallocenes and non-metallocene single-site catalysts. Even Dow's "constrained-geometry catalysts", where a bridge links cyclopentadienyl-type with non-cyclopentadienyl-type (e.g. alkylamido) ligands to form a half-sandwich complex with a titanium center [80, 81], to become the basis for DOW's INSITE™ technology and ENGAGE™ polyolefin elastomer product line, might thus be regarded as evolutions of the *ansa*-metallocene concept.

The role of *ansa*-metallocenes for the industrial production of i-PP (initially the primary aim of their development) is still limited to specialized niche applications with relatively small market shares and thus – ironically – is less important than for other polymers such as m-LLDPE. Besides the specifics of isotactic propene homopolymers and their applications in injection molding and BOPP, higher costs for the use of *ansa*-metallocene catalysts and rather severe patent hurdles have limited their full success in industrial i-PP production so far. However, LyondellBasell and Lummus Novolen Technology GmbH, the two active licensors of metallocene technology for the isospecific polymerization of propene, have both reported the development of highly active *ansa*-metallocene catalysts for i-PP, which reduces the cost gap between such catalysts and modern Ziegler–Natta catalysts [82, 83]. At the same time, many of the basic patents, by which access to *ansa*-metallocene technology for i-PP had been limited to only a handful of players, have now expired or will expire in the near future. It will be interesting to see whether this will finally open the path for a wider use of *ansa*-metallocene catalysts in the industrial production of i-PP.

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