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Catalysts for olefins polymerization

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Abstract

Polyolefins are still protagonist of an exciting innovation, due to a continuous development of new catalysts, processes and products. The positive solutions given by polyolefins to the environmental and energetic issues are among the factors responsible for their success. The most relevant breakthrough occurred in the last years is the discovery of metallocenes, and more in general, of single centre catalysts. They are, in most cases, highly active catalysts and are already employed on the industrial scale for the preparation of both "drop-in" products with improved properties, and of totally new materials. © 1998 Elsevier Science B.V. All rights reserved.

1. Polyolefins

Polyolefin plastics are nowadays in their mature phase, with a consumption of about 40 million tons per year, and could therefore be appropriately defined as "commodity".

However, recently they have been protagonist of an exciting innovation through a continuous development of new processes and products.

Such an exceptional expansion is mainly due to the following factors:

1. a great versatility in terms of properties, that makes them suitable to the most diverse applications;
2. the environmental aspects (polyolefins are absolutely non-toxic and friendly to the environment);
3. the superior saving in energy costs, both at production and application levels with respect to other conventional materials;
4. the low costs due to the plentiful availability of raw materials;
5. the possibility of adopting low cost, very versatile and non-polluting processes.

2. Environmental and energetic aspects

The most important factor governing the growth of chemical industry in the future years is likely to be its effect on the environment.

Nowadays, new materials have to be developed carefully considering the whole life cycle, from conception to destruction, with the aim of keeping the whole process environmentally benign at every step. In addition, each process involved should be carried out in an energy efficient manner.

The environmental problems have to be approached taking into consideration that the energy price is extremely likely to increase in the future.

As far as the plastic materials are concerned, although they amount to less than 10% of the total waste, they are a visible problem in the environment. This means that one of the most important factors related to plastic materials is their recycling. Three

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ways have been identified to face this problem, mechanical, chemical and energetic recycling, and a combination of these solutions will probably be the best approach. The energetic approach, that implies a burning process of the plastic material, in principle presents the most critical environmental impact. Considering the broad spectrum of polymeric materials used nowadays, their incineration can bring about different environmental problems, making it mandatory to simplify the plastic world.

Forecasts predict that the number of major plastic types will be reduced. Polyolefins could become as much as 70% of the thermoplastic polymers used by the year 2000.

A concentration of a single polymer class simplifies the recycling, and in the case of polyolefins, would produce relatively harmless gases and the energy could be recaptured through incineration. In addition, it is more convenient to burn the lower cost materials than recycling them, due to the balance between the energy recovery cost and the initial cost. In this respect, the best recovery value and energy saving will undoubtedly occur by using plastics in place of materials requiring more energy input.

In conclusion, environmental aspects will have a tremendous effect on the future development of the chemical industry. The best way for the industry to protect their products is to design processes that give a contribution to the solution of the environmental problems, especially as the ability of producers to work with highly toxic chemicals will be greatly reduced. New plants will be confined to manufacturing products using environmentally friendly processes as the marketplace is looking for products that are able to provide a higher standard of living in an environmentally conscious and safe world at lower prices.

Polyolefins are able to meet all these requirements.

3. The world of thermoplastic polymers

The penetration of polyolefins into the worldwide plastic market place in the last 50 years has been spectacular. In fact their market share was around 20% of the total thermoplastics market in 1960s while it is reaching almost 60% in the 1990s with an average growth rate around 10% per year.

4. High yield catalysts

The Ziegler–Natta catalysis has been the key factor for the realization of the outstanding development of polyolefins and is still playing a fundamental role for the innovation of the field. More and more sophisticated new catalysts have made possible advanced polymerization technologies, improved product grades and a broader range of applications.

The first high yield catalysts were obtained in [1] by co-milling $TiCl_3$ and $TiCl_4$ with $MgCl_2$. The crystalline form of $MgCl_2$ corresponds to a cubic packed stacking of double chlorine layers with hexa-coordinate interstitial Mg^{+2} ions. By reaction with titanium salts, the planes of chlorine atoms undergo translation and rotation, producing the destruction of the crystal order in the stacking direction. A disordered structure is formed and, as a consequence, a gradual disappearance of (1 0 4) reflection is noticed in the X-ray diffraction spectrum and a halo appears in its place. An increase of specific surface due to a reduction of crystallite size takes place.

As a consequence of this disordered structure, many Mg ions, coordinatively unsaturated and located at the edges and at the most probable cleavage surfaces, (1 1 0) and (1 0 0) planes, become available. In particular, these two lateral cuts show different local situations: Mg atoms with a coordination number 5 (1 0 0 cut) and 4 (1 1 0 cut). During the reaction (e.g. by co-milling) with titanium tetrachloride, a $TiCl_4$ molecule or Ti_2Cl_8 dimers may be epitactically placed on lateral surfaces of $MgCl_2$. This resulting structure is very important in the case of propylene polymerization. In fact, Corradini et al. [2], on the basis of evaluation of non-bonded interactions, demonstrated that epitactic placement of dimeric Ti_2Cl_6 (deriving from reduction of Ti_2Cl_8 with alkyl aluminium) on (1 0 0) face of $MgCl_2$ leads to the formation of stereospecific site whereas a non-stereospecific site results from coordination of $TiCl_3$ or Ti_2Cl_6 moieties on (1 1 0) face.

The catalyst system $MgCl_2$–$TiCl_4$/AlR_3 is endowed with a very high activity in ethylene polymerization. In the case of the propylene polymerization, the high activity is combined with a low stereospecificity (40–50%) because of the presence of both isospecific and aspecific sites on the catalyst. Montedison scientists [3], in early 1970s, discovered that it is possible to increase the stereospecificity of $MgCl_2$ based catalysts by using electron donors (EDs). Best results were obtained with two different EDs: the first placed on the solid component (the so-called inside donor, iED) and the second used together with AlR_3 (outside donor/oED). The most effective stereoregulating EDs are the following:

1. tetramethylethylenediamine (TMEDA); ethyl benzoate (EB); diisobutylphthalate (DIBP) as iED;
2. EB; methyl *p*-toluate (MPT); 2,2,6,6 tetramethylpiperidine (TMP); alkyl alkoxy silanes as oED.

An exchange between iED and oED occurs during the polymerization.

Possible explanations of the role of EDs are the following [4]:

1. selective poisoning and/or modifying of aspecific catalytic sites through their complexation with ED;
2. competition of ED with $TiCl_4$ for selective coordination of unsaturated Mg ions on different faces of $MgCl_2$;
3. taking into account that (1 0 0) faces are more basic than (1 1 0) faces as far as coordination to $TiCl_4$ is concerned, stereospecific titanium sites is located on the (1 0 0) faces and ED saturates the coordination vacancies of Mg atoms present on the (1 1 0) faces avoiding the placement of aspecific titanium on these planes.

The higher activity of $MgCl_2$ based catalysts with respect to traditional catalysts is due to a higher number of active sites and a higher propagation rate constant (K_p). In fact the percentage of active titanium in $TiCl_3$ based catalysts is around 1% of the total amount, whereas in high yield catalysts it is around 10%. Furthermore, the values of the propagation rate constants are one order of magnitude higher for $MgCl_2$ based catalysts.

An outstanding increase of productivity, control of stereospecificity and morphology has been obtained through a continuous improvement of high yield $MgCl_2$ based catalysts.

We have recently discovered new $MgCl_2$ based catalysts for PP production [5], containing a new family of internal donors belonging to the class of 1,3-diethers and having the general formula $(R_1,R_2)C(CH_2OR)_2$.

These catalysts are able to form, with high yield, highly stereospecific PP in the absence of any external donor.

The widely accepted mechanism of stereoregulation by Lewis bases, discussed above, is based on the competition of the Lewis base with $TiCl_4$ for a selective coordination on the unsaturated magnesium atoms available on the different lateral faces of $MgCl_2$. We believe that one of the most important feature of a bifunctional electron donor in propylene polymerization is the distance between the coordinating atoms, that has to be suitable for chelating on the tetracoordinate magnesium atoms located on the (1 1 0) face of $MgCl_2$. The results obtained with catalyst systems containing phthalate and silanes, both bifunctional bases, used as internal and external donors, respectively, strongly support the above model.

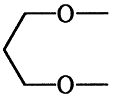
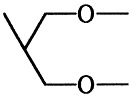
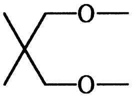
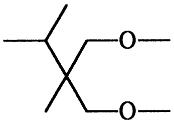
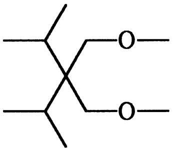
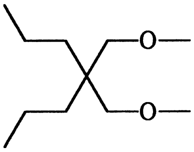
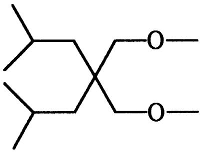
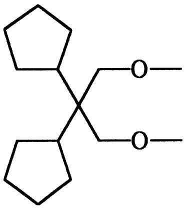
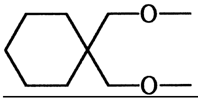
Through molecular calculation and conformational analysis it was possible to identify some diethers, in particular 1,3-diethers, characterized by the right distance between the coordinating atoms. These compounds, tested as internal donors in propylene polymerization, gave outstanding results in terms of activity and stereospecificity [6].

As a result of a very large experimentation it is possible to observe that when the maximum probability value for the oxygen–oxygen distance in a diether, determined according to Conformation Statistical Distribution methodology, is close to 3 Å, the catalyst performance is very good, whereas, when the distance values are spread out in a wide range, the performance is very poor (see Table 1).

These new catalytic systems, developed in the last few years, result in greatly simplified production processes. Many plant sections are no longer required, as, for example, catalyst removal, amorphous polymer separation, unreacted monomer purification, pellettization and effluents treatment.

These new simplified processes are thus more economic and reliable and, furthermore, are environmentally benign, as they do not produce any kind of effluent. They also offer broad flexibility, as shown by the range of molecular structures that can be produced:

Table 1
1,3-Diethers as internal donors in $MgCl_2$ supported catalysts

Donor	O–O distance (Å)	Productivity (Kg PP/g cat)	I.I. (%)
	2.9–4.7	4.0	64.9
	3.9–7.2	30.0	74.9
	2.7–4.8	35.0	89.8
	2.9	40.0	94.9
	3.0	42.0	96.4
	2.7–3.2	33.0	95.6
	2.8	60.0	96.9
	2.8	52.0	97.5
	3.4	25.3	89.0

Polymerization conditions: 4 l reactor; propylene 1.2 kg; hydrogen 1.7 NL; $AlEt_3$ 2.5 mmol/l, 70°C, 2 h. I.I.=xylene insoluble at room temperature.

- homopolymers, ranging from extremely low to extremely high molecular weight;
- random and heterophasic copolymers with different olefinic comonomers, with a wide range of performances.

In Table 2, the performance of catalysts belonging to different generations are reported.

5. Polymer architecture control

Using the $MgCl_2$ based catalysts for PP, developed by Montedison and endowed with controlled morphology and porosity, it is possible to achieve the control of the tridimensional structure of the catalyst particle and, as a consequence, of the obtained polymers. The control of the polymer architecture allows the synthesis of new materials with improved properties, as heterophasic olefin copolymers, polyolefin alloys (catalloy) and polyolefin alloys with non-olefinic polymers, from a technology called by Montell as Hivalloy [7].

6. Heterophasic olefin copolymers

Heterophasic polypropylene copolymers are tough, high impact materials with polypropylene as the continuous phase and an elastomeric phase (usually an ethylene–propylene rubber) uniformly dispersed within the matrix. The rubbery phase must be homogeneously dispersed and its size controlled in order to achieve the best stiffness-impact balance. Looking at a cross section of a heterophasic polypropylene copolymer it is possible to see that EPR rubber particles are clearly uniformly dispersed in the polypropylene matrix.

Before the discovery and the commercial exploitation of the high yield $MgCl_2$ based catalysts, the heterophasic copolymers, with a high rubber content, were essentially prepared by melt blending, in an extruder, the preformed polymers. This technology brought about significant limitations on the properties of the polymers to be blended. For instance, a strong difference of melt viscosities of the various components of the blend prevents from the formation of EPR domains of appropriate size.

Table 2
Performance of catalysts belonging to different generations

Generation	Catalyst system	Productivity (kg PP/g cat)	I.I. (wt%)	Morphology
First	$TiCl_3$ $0.33AlCl_3$+DEAC	2–4	90–94	Powder
Second	$TiCl_3$+DEAC	10–15	94–97	Granular
Third	$TiCl_4$/Ester/$MgCl_2$+AlR_3/Ester	15–30	90–95	Spherical
Fourth	$TiCl_4$/Diester/$MgCl_2$+TEA/Silane	30–60	95–99	Spherical
Fifth	$TiCl_4$/Diether/$MgCl_2$+TEA	100–130	96–99	Spherical

Polymerization conditions: bulk, 70°C, 2 h.

To prepare the optimum heterophasic polymer structure, directly in the polymerization reactor, it is important to tailor the catalyst, not only in view of the structure of the macromolecular chain but also aiming at the appropriate relative distribution of the different polymeric phases, i.e. the crystalline polyolefin and the polyolefin elastomer. One of the most important concept developed in 40 years of research in Ziegler–Natta catalysis from Himont/Montecatini is the ‘‘Reactor Granule Technology’’.

7. Reactor Granule Technology

The Reactor Granule Technology can be summarized as follows: a growing, spherical polymer granule provides a porous reaction bed where other monomers can be introduced and polymerized to form a polyolefin alloy.

The basic requirements for a high yield catalyst suitable for Reactor Granule Technology are the following:

1. High surface area.
2. High porosity.
3. Mechanical strength high enough to withstand mechanical processing, but low enough to allow the forces developed by the growing polymer to break down the catalyst into microscopic particles that remain entrapped and dispersed in the expanding polymer particles.
4. Homogeneous distribution of active sites.
5. Free access of the monomers to the innermost regions of the catalyst.
6. Maintenance of above characteristics with a range of different monomers.

The control of the polymer particle morphology has major relevance on the economics and feasibility of the polymerization process.

The phenomenology of the polymer particle growth is rather complex [8]; the basic principles of this growth process are:

1. each catalyst particle gives rise to a polymer particle;
2. the polymer particle replicates shape and type of particle size distribution of the catalyst particle;
3. the average particle size replication factor depends on the catalyst activity and approximates to 20–30 times for high activity catalysts;
4. according to the most accepted model, the ‘‘multigrain’’ model, during polymer particle growth the catalyst particle disintegrates and the fragments become dispersed throughout the whole polymer particle.

This model, that considers both transport phenomena within the particle at two distinct levels (micro- and macroparticle) and external boundary layer gradients (temperature and concentration), has found many experimental confirmations.

8. Catalloy

The research on the Reactor Granule Technology has opened new possibilities in the field of polyolefin alloys.

The Catalloy process allows unique reactor-made polymeric compositions endowed with properties no longer limited by mechanical considerations.

Such a process is a new and highly sophisticated technology, based on three mutually independent gas-phase reactors in series. Its versatility is suitable to design special polymeric compositions able to meet today's existing polyolefin applications and to face tomorrow's developments.

Broader MWD, higher stereoregularity, random copolymers containing up to 15% of comonomers and heterophasic alloys containing up to 70% of multimonomer copolymers are achievable.

No by-products are produced and no operating fluids are requested, with significative economical and ecological advantages.

9. Hivalloy

The Reactor Granule Technology makes also possible an exciting new technical frontier, allowing the incorporation and polymerization of non-olefinic monomers in a polyolefin matrix. The porous polyolefin granule gives a very high specific surface area and a very high reactivity substrate suitable for easy reaction with non-olefinic monomers at a level greater than 50 wt% via free radical graft copolymerization.

Himont called this emerging technology Hivalloy and the combining of non-olefinic monomers with an olefinic substrate makes possible a family of materials not commercially achievable previously. These resins are expected to bridge the performance gap between advanced polyolefin resins and engineering plastics, and are therefore, truly "Specialty Polyolefins".

A first target of the Hivalloy family of products will be those applications currently served by ABS. Possessing both olefinic and non-olefinic characteristics, Hivalloy products are designed to combine the most desirable properties of PP, such as processability, chemical resistance and low density, with many of desirable features of engineering resins which cannot be achieved with currently available polyolefins, such as improvements in the material's stiffness/impact balance, improved mar and scratch resistance, reduced moulding cycle time and improved creep resistance. Because of their olefinic base, Hivalloy polymers readily accept minerals and reinforcing agents, providing added flexibility and control over properties further expanding the PP property envelope into the specialty area.

10. Metallocene based catalysts (MBC)

The most relevant breakthrough occurred in Ziegler–Natta catalysis over the last years is the discovery of the *metallocene/alumoxane* catalysts [9].

Metallocenes are pseudotetraedric, d^0 organometallic compounds, with two cyclopentadienyl ligands (Cp) η^5 coordinated to a transition metal: in the case of Ziegler–Natta catalysis, the transition metal is typically titanium, zirconium or hafnium. The general formula Cp'_2MX_2 can be used to describe these compounds. The Cp ligands can be substituted by alkyl, alkenyl, aryl and alkylaryl groups, with fused aromatic or aliphatic rings and bridged through carbon, silicon and germanium atom. The "X" ligands derive either from halogen atoms (typically chlorine) or from hydrocarbons (e.g. methyl or *n*-butyl groups) or from alcohols (e.g. α-binaphtol).

These complexes were already used by Natta et al. and Breslow and Newburg in 1950s (see [10]), in combination with aluminum alkyls, for ethylene polymerization, obtaining extremely low catalytic activities.

At the end of 1970s, Sinn and Kaminsky (see [9]) combined the metallocenes with a new cocatalyst, polymethylalumoxane (MAO), obtaining, with very high catalytic activity, polyethylene and low molecular mass atactic polypropylene.

MAO is the product of a careful reaction between trimethylaluminum and H_2O. The water source is generally a hydrated inorganic salt, as $Al_2SO_4 \cdot 16H_2O$, $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$ [11]. From many different analytical investigations, cryoscopic measurements, GPC and NMR analysis, one can hypothesize that MAO is composed of a mixture of linear and cyclic oligomers, containing a relevant amount of coordinated trimethylaluminum [11,12].

10.1. Metallocene based catalysis

The activating effect of MAO, that leads to the formation of active catalytic species, is considered occurring through the following pathway:

1. X ligand abstraction and alkylation of the transition metal;
2. stabilization of the resulting cationic species;

3. prevention of the bimolecular reduction of the transition metal.

The active species is a dicylopentadienyl alkyl cation.

It is important to underline that the π-ligands remain coordinated to the transition metal also after the reaction with MAO, thus affecting the catalytic activity, the propagation/chain transfer reaction rates, the stereospecificity of the polymerization and the relative reactivity of the comonomers in the case of copolymerization.

Looking more in depth into the chemistry of MBC, significant analogies but also remarkable differences can be identified with the traditional titanium based chemistry.

Among the former ones, it has to be mentioned that both titanium and metallocene based catalysis give rise to insertion polymerization, that can be classified as a coordinated ionic reaction with the transition metal bearing a partial positive charge and it occurs through a cis coordination of the olefin on the catalytic site.

The most important differences can be summarized as follows:

1. Metallocenes are organometallic compounds that can be completely characterized, both from the chemical and the structural point of view.
2. They are soluble in aliphatic and aromatic solvents.
3. The transition metal atom has a pseudotetraedric configuration in the case of MBC, whereas the titanium atom on the surface of $MgCl_2$ has an ottaedric configuration.
4. The electronic and steric surround of the catalytic centre can be much more easily modified in the case of MBC.
5. The chain growth mechanism implies two coordination sites in the case of MBC, while only one is available for the titanium anchored on the $MgCl_2$ surface.
6. The homogeneity of the catalytic centres, in the case of MBC (single-centre catalysts), allows the preparation of polymers with narrow distribution of molecular mass and chemical composition. These concepts can have an extensive application in the case of MBC, both for homo and copolymers. In fact, in the case of the homopolymerization of an 1-olefin to an essentially stereoregular polymer, the same catalytic centre is able to promote both the regular and the irregular insertion of the monomer. Thus, the regio- or stereo-irregular unit is statistically distributed along the macromolecular chain, as for the 1-olefin distribution in the copolymerization. As a consequence, the irregular unit can be seen as a comonomer. This is a substantial difference with the heterogeneous titanium based catalytic systems, that show a distribution of catalytic centres, some of them giving rise to an essentially stereospecific propagation and some others to aspecific polymerization.

10.2. 1-Olefins polymerization

The polymerization of 1-olefins, particularly of propylene, allows to highlight some of the most important features of MBC: first of all, their versatility, demonstrated by the capability to produce atactic, isotactic, syndiotactic, hemiisotactic and thermoplastic–elastomeric polypropylene and furthermore, the chance to establish a correlation between the symmetry of the metallocene and the tacticity of polypropylene. According to very recent results, this is true provided that the monomer concentration is not as low as to allow the occurring of reactions, as the epimerization of the growing chain, that lead to a decrease of the stereoregularity of the polymer. Disregarding the influence of the monomer concentration in the further discussion, the mentioned correlation can be summarized as in Table 3.

As reported in Table 3, freely rotating non-bridged metallocenes, also with substituted Cp ligands (e.g. Ind_2ZrCl_2), endowed with C_{2v} symmetry, give atactic polypropylene at conventional polymerization temperature.

Table 3
Correlation between metallocene symmetry and poly-1-olefin tacticity

Symmetry	Formula	Poly-1-olefin tacticity
C_{2v}	Cp_2ZrCl_2, $Cp_2^*ZrCl_2$	Atactic
C_2	Rac-EBIZrCl_2	Isotactic
C_s	$Me_2C(Cp)(Flu)ZrCl_2$	Syndiotactic
C_1	$Me_2C(MeCp)(Flu)ZrCl_2$	Hemiisotactic

Cp=cyclopentadienyl; Cp*=pentamethylcyclopentadienyl; rac-EBI=racemic-ethylenbisindenyl; Flu=fluorenyl; MeCp=3-methylcyclopentadienyl.

It is worth noting that some metallocenes belonging to the above mentioned classes are able to produce partially isotactic polymer at low polymerization temperature, as e.g. Cp_2TiPh_2 and $(RCp)_2MCl_2$ [13].

In fact, the rotation of the cyclopentadienyl rings makes impossible the C_2 symmetry required for an isospecific chain propagation. To prevent this rotation, the two ligands can be linked with $-C_2H_4-$, $-SiMe_2-$ or $-CMe_2-$ bridges that are able to make the metallocene stereorigid.

In 1984, Ewen [13] obtained a mixture of atactic and isotactic polypropylene using a mixture of the meso and racemic isomers of a stereorigid metallocene: ethylene-bis-indenyl titanium dichloride (meso/rac $EBITiCl_2$). This was the first direct evidence that a stereoregular polyolefin is obtained from a racemic catalyst. Kaminsky (see [14]), using the hydrogenated homologous zirconocene in the pure racemic form (rac-$EBTHIZrCl_2$), prepared by Brintzinger, obtained with a high yield isotactic polypropylene and poly-1-butene.

This key discovery led to a number of studies in which it was shown that both

1. the substituents present on the Cp rings, i.e. type, position and number of substituents, and
2. the transition metal, i.e. Ti, Zr or Hf,

directly dictate catalyst activity, degree of isotacticity and average molecular mass.

iPP produced with the mentioned EB(TH)I-type metallocenes has a very narrow MMD (1.8–2.2, compared with 4–8 from heterogeneous catalysts) and melting points 20–30°C lower than the conventional iPP. The low melting points are likely due to the generally low degree of isotacticity (% isotacticity 70–95%) and not perfect regiospecificity (0.5–2% tail-to-head units) achieved with chiral stereorigid metallocenes.

However, iPP's melting at 160–162°C have been obtained by proper alkyl substitution of the bridged-bis cyclopentadienyl zirconium framework. Two main classes of metallocenes can be identified:

1. bridged indenyl type, substituted by alkyl groups in position 2 and by alkyl or aryl groups in position 4 and optionally 6 [15];
2. bridged indenyl type, substituted by alkyl groups in position 2 and with a phenyl group condensed in positions 5 and 6 on the indenyl ligand [16].

Syndiotactic polypropylene was obtained by Ewen et al. [17] by using isopropyliden (cyclopentadienyl) (9-fluorenyl)MCl_2, metallocenes with C_s symmetry. It is worth noting that Ewen's catalyst is the first syndiospecific catalyst operating with site control, i.e. it is the chirality of the active species that orients monomer insertion as in the case of isospecific catalysts.

Syndiospecificity is remarkably high even at high polymerization temperatures.

When the metallocene symmetry is destroyed by adding a methyl group on the Cp ligand (as in Me_2C(3-MeCp)(Flu)$ZrCl_2$), the resulting polymer has a hemi-isotactic structure, i.e. only every other methyl group in the polymer chain is in an isotactic placement, the remaining methyls being placed at random [18].

The obtainment of this particular microstructure provided a confirmation of the polymerization mechanism of 1-olefins with metallocene catalysts: in the electrophilic tetrahedral $Cp'_2M\text{-}R^{(+)}$ active species, the olefin coordinates at the available site and the growing chain migrates to the olefin, with concomitant breaking of the double bond and formation of a new metal–carbon bond at the previously vacant site (chain migratory insertion).

Thus, there is a site-switching of the growing chain at every monomer insertion, and it is the chirality of the active site (with two active sites per metallocene molecule) that determines which monomer enantioface is inserted, through steric interactions between the monomer substituent and the Cp'_2M-growing chain framework.

10.3. *Ethylene/1-olefins copolymers from metallocenes*

Among the typical features of the metallocene based catalysis reported above, the homogeneity of the catalytic centres suggests the great potentiality of metallocenes as catalysts for ethylene and 1-olefins copolymerization. In fact, a narrow distribution of the molecular properties, i.e. molecular mass and particularly chemical composition, is highly desired for improving the properties of a copolymer.

A summary of the main molecular characteristics of copolymers prepared with metallocenes is reported in Table 4, with particular reference to polymers having an 1-olefin content enough to impart elastomeric properties to the material [19].

Table 4
Ethylene/1-olefin copolymers from metallocenes based catalytic systems

Max. catalytic activity (kg Pol/g Mt)	1600
1-Olefin (mol%)	15–50
Molecular mass, I.V.[a] (dl/g)	1.5–20
Molecular mass distribution, Mw/Mn	2–8
Chemical composition (%)	±2
Distribution[b]	
1-Olefin sequences	
Tacticity	Iso-, syndio-, a-tactic
m Diads (%)	100, 0, ~30
Regioirregularities	Absent or present
Copolymerizations	
Model	Bernoullian, first-, second-order Markovian

[a] Measured in tetraline at 135°C.
[b] Determined by fractionation.

From the data collected in Table 4, it can be concluded that metallocenes are able

1. on one side to impart some typical characteristics to the copolymers, as the narrow molecular mass distribution and the narrow intra- and intermolecular distribution of chemical composition and comonomer sequence;
2. on the other side to prepare many families of copolymers, that differ from each other as far as molecular mass, relative reactivity of comonomers, product of reactivity ratios, stereo- and regio-regularity of 1-olefin sequences are concerned.

Thanks to the narrow distribution of chemical composition and comonomer sequences, mentioned in (a), it is possible to define a single centre statistical model for the copolymerization. In agreement with what is reported in (b), different models, from bernoullian to second order markovian, can be used to describe the copolymerizations.

In conclusion, the expression *copolymers from metallocenes* has a meaning only if referred to the characteristics reported in (a). When mentioning the copolymers properties indicated in (b), that actually represent the true copolymers fingerprint, the said expression is misleading, representing an undue and incorrect summary of a complex world made of many different subjects.

10.4. Industrial exploitation of MBC

These results are just an example of the potentiality of MBC and allow also to envisage possible industrial applications of great interest.

An enormous research activity burst after the first discoveries, both in the academic and in the industrial world. According to the Stanford Research Institute, the global expense for the research activities in the field of metallocenes is so far about four billion dollars. All the important companies active in the field of polyolefins are involved in this effort: Exxon, Hoechst, Fina, BASF, Dow, Idemitsu, Mitsui Toatsu, Mitsui Petrochemical and Montell.

The importance of MBC, in view of an industrial exploitation, can be summarized as follows:

1. All the traditional polyolefins can be prepared, often endowed with improved properties.
2. New polymers were already prepared. The most important are the following: (a) highly syndiotactic poly-1-olefins: polypropylene, poly-1-butene, poly-1-pentene, poly-4-methyl-1-pentene, polyallyltrimethylsilane; (b) atactic polypropylene with high molecular mass; (c) ethylene and propylene copolymers with 1-olefins, crystalline and amorphous, with new microstructure and physical–mechanical properties.
3. A more fruitful exploitation and even a simplification of the existing industrial processes can be envisaged.

To allow an industrial development for the metallocenes based catalysis, a couple of drawbacks appeared since the beginning as the main ones:

1. the use, in large amount, of an expensive cocatalyst as MAO;
2. the "homogeneous" nature of metallocenes, that does not allow their use for bulk and gas phase polymerizations.

To solve the first problem, we have developed in Montell, alternative, MAO-free cocatalytic systems based on branched aluminum alkyls [20].

To have the chance of using the metallocenes in the mentioned processes and to control the morphology of the obtained polymers, the way followed was the supportation of MBC on a carrier.

10.5. Supportation of MBCs

Many scientific papers and patents report attempts of supportation of the components of the catalyst system on different carriers: SiO_2, Al_2O_3, $MgCl_2$ and polymers were the most investigated. In general, the transition metal compound, MAO and the carrier were reacted with different combinations and the resulting catalyst is employed in propylene polymerization with a common trialkylaluminum as a co-catalyst.

In a recent paper, Soga has demonstrated that, when the metallocene is immobilized on a chemically modified silica, it can be activated by ordinary trialkylaluminum to give isotactic polypropylene with a totally MAO-free catalyst system. In particular, a $=SiCl_2$ functionalized silica is further reacted with a Li salt of a cyclopentadienyl-type ligand to give a metallocene linked through its bridge.

We have developed in Montell a technology for the supportation of polymers, as crosslinked polystyrene [21] and porous polyethylene and on $MgCl_2$ [22]. The catalytic activity and the investigated copolymer properties were found to be unchanged after the supportation of the metallocene on the mentioned carriers.

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