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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

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Compiling & Editing: J. Roetzer-Sweetland
Editorial Board: V. Podshibyakin, G. Ramsey, G. Anestis

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Tel.: + 43 1 21131-0 Fax: + 43 1 21131 6843
Email: jroetzer-sweetland@unido.org
OR vkozharnovich@unido.org
INTERNET: http://.www.unido.org

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Dear Reader

The discovery of metallocene catalysts has led to dramatic changes in the polyethylene industry. A new class of polymers is available with properties never thought possible in the polyolefin business. The unique possibility of tailoring a catalyst according to need, make metallocene catalysts a versatile and valuable tool in the hands of chemists and product developers.

An important characteristic of metallocene polymers is the increased toughness and mechanical strength that they possess. This property can lead to improved products, or it can be used to reduce the amount of polymer needed to manufacture a part. Thus, raw materials can be reduced. This could well have an impact on the overall consumption of oil in the future.

More importantly, metallocenes not only offer improved, but new properties. An important application in developing countries, might be the use of 'breathable' packaging for prepared products. Vegetables packed in metallocene polyethylene films stay fresher for a much longer period than if they were packed in ordinary films. This could result in a better food supply, since shipping problems by spoiling are reduced.

Today, metallocene products have achieved a very small share of this market, but this is destined to change as the major alliances drive down costs to deliver product performance for volume rather than niche applications. By the year 2005, metallocene products are estimated to count for 12 per cent of the polyethylene market. Opinions vary on how quickly metallocene products will have an impact on polyethylene markets.

Taking this into account, UNIDO has decided to draw the attention of those dealing with new product and business development in the area of new materials, and who may well find a niche in this emerging market. Your feedback is, as always, very welcome!

Vladimir Kozharnovich,
Technical Editor

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A. SPECIAL ARTICLE

METALLOCENES — FROM A LABORATORY CURIOSITY TO INDUSTRIAL-SCALE APPLICATIONS

by Dr. Marc Oliver Kristen

Introduction

In the last few years a new class of catalysts has received a lot of attention in the production of polyolefins. While chromium (Phillips) and titanium (Ziegler/Natta) catalysts have been widely used in the polyolefin industry since the 1950s and 1960s it took until the 1990s for a new type of catalyst to be applied to the industrial scale. Unlike the two conventional catalysts that are "multi-site" catalysts the new metallocene catalysts provide only a single active centre that can be tuned by altering the ligand sphere of the central atom. With the use of these "single-site" catalysts it is now possible to obtain uniform polymers with controlled properties.

This article gives an introduction to this exciting and challenging field of catalysis research. It covers the basics of metallocene chemistry, supported catalysts and their application to industrial scale polymerization. The differences of the new polymers in comparison with existing polymers will be shown. Based on this information the advantages of the new polymers will be demonstrated in various applications. The article will also give a survey of the major industrial players in this field and an outlook about the expected development of metallocene based polymers. The effect that this new technology may have on developing countries will also be described.

Metallocene Chemistry

History

Metallocenes are special members of a class of chemical substances known as organometallic compounds. These compounds combine metal atoms in various oxidations states with an organic environment. In organometallic chemistry this environment is called ligand sphere. This ligand sphere can consist of one or more different organic compounds (ligands). In classical metallocenes the central metal atom is surrounded by two cyclopentadienyl (cp) ligands. Due to their structure these compounds have been named "sandwich complexes". Organometallic compounds bearing only one cp-ligand are known as "half sandwich complexes". Although not genuine metallocenes, they are also generally referred to as metallocenes (see figure 1).

The first metallocene (ferrocene, with an iron atom as central atom) was synthesized in the 1950s. Its unique structure was determined shortly after its synthesis and led to the award of the Nobel Prize to Fischer and Wilkinson in 1973.[1] Also in the 1950s Ziegler and Natta discovered the polymerization of α-olefins with titanium/aluminium catalysts (Nobel Prize 1963).[2]

These two major discoveries triggered the explosive growth of organometallic chemistry since then. In 1957 the first reports about polymerizations of ethylene with cp_2TiCl_2 a bent-sandwich metallocene were published.[3,4] In these polymerizations the same aluminium compound (diethylaluminiumchloride) was used as a cocatalyst that was generally applied to heterogeneous Ziegler/Natta catalysts. The use of aluminium alkyl compounds as cocatalysts is necessary to transform the metallocene dichloride (e.g. cp_2TiCl_2), which itself is not active in polymerizations to the catalytically active form.

MAO activation

Although many attempts have been made to increase the activity of this system, it took until 1980 when Sinn and Kaminsky discovered that traces of water in the halogen free system cp_2TiMe_2/aluminiumtrimethyl could greatly enhance the performance of the system.[5,6] With the careful addition of water to aluminiumtrimethyl a new substance called methylalumoxane (MAO) had been synthesized for the first time. This new compound cannot be described as a single molecule but as a mixture of chains and rings that consist of the repeating unit (-O-Al(CH_3)-). In spite of the efforts that a lot of research groups spent to reveal the secret of MAO its exact structure is still unknown. The mechanism of the activation of metallocenes with MAO is described in figure 2.

It is believed that MAO alkylates the metallocene and then abstracts one of the methyl groups to generate the catalytically active species: The metallocenium cation. The balance of the three properties—alkylation of the metal atom, abstraction of a methyl group and stabilization of the created metallocenium cation without reacting with it—made MAO a unique tool and the cocatalyst of choice in metallocene activation.

In addition, Sinn, Kaminsky and co-workers discovered that zirconocene catalysts show a much better temperature stability compared with titanocene catalysts which decompose above 0° C.[6]

Activation with boron compounds

Although the use of MAO (generally employed in hydrocarbon solution) was the breakthrough in metallocene activation, this method has some disadvantages. First of all, MAO has to be used in a very large amount. Generally, a couple of hundred to more than ten thousand equivalents have to be used in order to get high productivity catalysts. Therefore, and since the synthesis of MAO is rather difficult, MAO is very expensive. Second, due to content of aluminium-carbon bonds, MAO is pyrophoric and reacts very violently with water and air. It is a dangerous compound to deal with, especially when larger amounts or concentrated solutions are handled. Last but not least, as described above, MAO is a mixture of a variety of molecules. It is therefore difficult to get the same MAO again with each synthesis. Since the performance of a metallocene depends a lot on the MAO that is used, problems with reproducibility may occur.

With specially designed boron compounds[7,8] it is also possible to stabilize the metallocenium cation, after it has been generated by methyl group abstraction. These catalysts show the same activity as MAO activated catalysts without the disadvantages described. Here only one equivalent of activator is needed, the boron compounds are not pyrophoric and, even though not cheap chemicals, they are cost-competitive (see figure 3).

The major disadvantage of this class of compounds is that metallocene catalysts activated with them are very sensitive to impurities during the polymerization process. A careful comparison is therefore needed before applying the one or the other method to industrial-scale production.

Propylene polymerization

With zirconocenes it was possible to polymerize propylene and higher α-olefins, which was impossible to do with titanocenes.[6] Although the high stereoselectivity of the standard Ziegler/Natta systems could not be achieved with these first systems, a major breakthrough had been made. Combining these discoveries with the virtually unlimited possibilities of organic chemistry for the synthesis of new ligands for metallocenes, the door to a new field in olefin polymerization was wide open.

Some special metallocenes were prepared at that time[9] and were the subject of major investigations.[10,11] The ligand framework of these new *ansa*-metallocenes consists of two indenyl ligands (cp-ligands with a fused benzene ring) that are linked by a bridge. This means that the ligand sphere can be fixed in a certain geometry providing a chiral metal centre. Propylene polymerizations with catalysts of this type indeed yield highly isotactic polymers. These observations lead to thorough investigations of the questions as to which mechanism controls the stereochemistry of the polymer growth and what influence the different metallocenes will have on tacticity and other properties of the polymers obtained with them. Figure 4 shows how variations in the ligand sphere of metallocenes can lead to different polymers.

One problem that comes along with the use of these chiral metallocenes to produce isotactic polymers is that the synthesis of the metallocenes generally yields a mixture of the desired racemic (rac) form and the meso form that will not produce the desired isotactic polymer. Therefore, the meso form has to be separated from the rac form in order to obtain a highly isotactic polymer (see figure 5).

Syndiotactic polypropylene, obtained by metallocene catalyst as described above,[12] is not a completely new polymer, as it had been isolated by Natta and co-workers[13] in 1962, but it had never been produced on a commercial scale. Due to its syndiotacticity it can not crystallize completely. Its slow crystallization behaviour prevented commercial applications until now, although trial runs in commercial-scale reactors have been reported by Fina.

In addition to the stereoselectivity the structure of the ligand sphere also influences the regioselectivity. A propylene molecule can be inserted into the growing polymer chain by three ways:

1. 1-2 (or head to tail) insertion, the "normal" insertion mechanism;
2. 2-1 (or head to head) insertion and;
3. 1-3 insertion, a chain straightening.

As can be seen in figure 6, the type of metallocene used for propylene polymerization has a significant impact on the way a propylene is inserted in the polymer chain. The influence on the bulk properties of these polymers will be described later in this article.

Ethylene polymerization

A important feature of polyethylenes is the amount of comonomer that is incorporated in the polymer. For certain reasons that will be described later, it is important to have metallocene catalysts that incorporate comonomers such as butane, hexane or octane very well. The catalyst's structure determines whether an ethylene/α-olefin-copolymer contains a lot or just a little of comonomer at a given comonomer concentration in the polymerization reactor. Here the crucial point is the angle between the two cp rings. If the angle is small the "metallocene mouth" is rather closed, while a large opening angle means a wide open "mouth" that is ready to consume larger olefins (such as hexane and octane) much more easily. Single cp complexes where one cp ring has been replaced by another group (e.g. amido group)[14,15] can be seen as metallocenes with only an "upper jaw". They have a very wide opening angle and are therefore very well suited to incorporate large amounts of comonomers (see figure 7).

Control of molecular weight

Another point where the ligand can have an impact on the polymer structure is the molecular weight. It is possible to increase the molecular weight of the polymer dramatically just by adding one substituent at the right place. Figure 8 shows a typical example.

Control of block structure

Recently Waymouth and co-workers[16] discovered a class of metallocenes where the block structure of polypropylenes can be controlled by the ligands of the metallocene. The (2-phenylindenyl) zirconium dichlorid complex oscillates between a chiral and an achiral form. While the chiral form produces isotactic polypropylene, the achiral isomer forms an atactic polymer. Since these isomers can be transformed into each other, the resulting polypropylene is an atactic-isotactic-stereo block polymer with elastic properties. The ratio of atactic and isotactic blocks is determined by the interconversion of the different forms into each other and therefore depend on the temperature. Polymers of this type are only accessible via metallocene catalysts (see figure 9).

(Co-)polymerization of other monomers

Metallocenes do not only allow the direct control of properties of polyethylene and polypropylene, but also enable the synthesis of polymers with new monomers that could not been copolymerized with olefins until now. In addition, novel polymers starting with standard monomers can be obtained using metallocenes.

With Phillips and Ziegler/Natta catalysts only α-olefins with eight or less carbon atoms could be copolymerized with ethylene in commercial scale. Metallocenes do not have these limitations and can copolymerize ethylene with higher α-olefins. New polymers include syndiotactic polystyrene[17] and poly(isocyanate)[18] (see figure 10).

Unlike conventional atactic polystyrene that is polymerized radically or ironically, syndiotactic polystyrene (s-PS) is only obtainable via metallocene catalysis. Because of its high melting point and resistance to chemicals it is expected that it can be used as a heat resistant or engineering material e.g in the automobile industry. Potential applications include high module fibres and microporous membranes. s-PS has recently been introduced commercially by Idemitsu Kosan and Dow Chemical under the trade name Questra.[19]

Substitution of one Cl-ligand by a trifluoroethoxy group allows the polymerization of isocyanates to Nylon-1. Still, metallocene catalysts have not found any applications in this field yet.

As Okuda and co-workers have shown, monocyclopentadienyl titanium complexes even allow the living ring-opening polymerization of ε-caprolactone, that means every titanium centre initiates one chain[20] (see figure 11).

Organolanthanoide complexes allow the polymerization of a wide variety of polar monomers.[21a-c] Recently zirconocenes have been found to polymerize methyl methacrylate, too.[21d] Syndiotactic poly(methylmethacrylate) shows good properties as an optical disc material. The introduction of polar functional groups into polyolefins by copolymerization of, for example, ethylene with MMA or ε-caprolactone is very attractive as new engineering plastics with applications like adhesion resins, or printable or dyeable resins result. Additionally, degradable copolymers can be polymerized from ε-caprolactone, hydroxy butyrate and ethylene glycol (see figure 12).

Metallocenes furthermore allow the polymerization of cyclic olefins such as cyclopentene without ring opening. The extremely high melting point of this new polymer makes processing difficult, and therefore copolymerization of cyclic olefins with, for example, ethylene is preferred.[22,23] These resulting amorphous cycloolefin copolymers (COC) show high transparency, very low uptake of moisture and ultimate resistance to chemicals which makes them very interesting as optical and high-impact materials (e.g. for compact disks, where polycarbonate is used). The first commercial product has been introduced recently by Hoechst and Mitsui Petrochemical under the brand name Topas[24] (see figure 13).

Metallocenes also allow the enantioselective synthesis of chiral polymers for the first time (e.g. the cyclopolymerization of 1,5-Hexadiene)[25,26] (see figure 14).

Non-polymer related use of metallocenes

The cpM- or cp_2M-fragment represents a reactive metal centre embedded in a stable and structurally defined template, where the conversion of an organic substrate in many cases proceeds with outstanding chemo-, stereo- and enantioselectivity. Examples include various olefin transformations, C-C- and C-X-coupling reactions as well as hydrogenations.[27]

Olefin transformations:
- Hydrogenation
- Isomerization
- Hydroamination
- Hydrosilylation
- Hydroboration.

C-C coupling reactions:
- Ethylmagnesation
- Cyclisation
- Olefin insertion/en route.

C-X coupling reactions:
- Cyclization of Aminoolefins.

Summary

The systems described above deal with a large variety of monomers and show that metallocenes are a versatile tool for polymerizations. Some of the polymers described are still curiosities and at their early stages of development.

In contrast, polyethylene and isotactic polypropylene are already manufactured with the new generation of catalysts. This article will therefore focus on these two types of resins. Especially polyethylene will be described in detail since the development of this polymer is most advanced.

Polymerization processes for polyolefins

To make use of the new polymers the metallocene catalysts have to be applied on a commercial scale. Since the development of a new polymerization process is very expensive and needs a long time, fast penetration of the market with the new polymers requires the use of already existing production plants. The processes for the manufacturing of polyolefins can be roughly divided into four groups:

1. **High-pressure process (only for polyethylene):**

Ethylene is polymerized at pressures of 1500-3000 bar and temperatures of 200-300° C. So far, metal complexes had been used only very rarely as catalysts. Standard radical starters are oxygen or peroxides. Under the conditions described, the ethylene is in its supercritical (liquid) phase. Two basic types of this process are known: (stirred) autoclave and tubular reactors.

2. **Solution process (only for polyethylene):**

The polymerization generally takes place in (high boiling) hydrocarbon solutions at temperatures from 160-200° C at pressures up to 300 bar.

3. **Slurry process**

As the name indicates, the polymerization is performed in a two-phase system. The suspension reagent is a low boiling hydrocarbon (in case of polypropylene it can also be propylene itself). Typical reactor conditions for a Phillips loop reactor (polyethylene) are 40 bar and 70-110° C. The catalyst has to be supported on a suitable carrier (e.g. silica) in order to prevent the formation of chunks and coating of the reactor walls by the polymer (so called reactor fouling) and to control the polymer morphology. Homogeneous catalysts will not lead to an operable reactor.

4. **Gas phase process**

Here the polymerization is run in vapour phase. As in the slurry process, the catalyst has to be supported. One differentiates between stirred gas phase (e.g. Novolen process for polypropylene (BASF)) and fluidized bed reactors (e.g. Unipol (Union Carbide Chemical)) and **Innovene** (BP Chemical) processes for polyethylene). Reactor conditions are generally 20-40 bar and temperatures of 70-115° C. The gas phase technology is supposed to be the most modern process, since it avoids the use of any solvent or suspension reagent and requires only moderate pressure and temperatures. Although difficulties in the use of gas phase reactors arise from electrostatic problems and control of heat removal from the polymer particles, it is believed that most of the newly installed reactors will be gas phase reactors. Implementation of metallocene catalyst in the process is therefore inevitable.

Supported metallocene catalysts

Since most of the production plants for polyolefins are based on one of the heterogeneous processes described above, it was necessary to develop a method to support the homogeneous metallocenes. The goal was to provide a system which controls the polymer morphology and prevents reactor fouling and at the same time reduces the large amount of MAO that is required to activate the metallocenes.

One route developed to overcome the last problem involves the generation of cationic metallocene complexes with the aid of the above-mentioned non-coordinating boron compounds. However, this approach does not allow for any control of polymer morphology. Another possibility involves the immobilization of metallocene compounds on a support, as is well known in Ziegler/Natta and Phillips catalysts. In this case, the aim is to find a way to attach the metallocene to the support without losing the performance of the homogeneous complexes (high catalytic activity, stereo- and regiochemical control, homogeneous comonomer incorporation, etc.) while improving the morphological characteristics of the polymers and the metallocene activation step in order to meet the requirements for industrial applications.

The development of supported metallocenes will enable their use in slurry- and gas-phase processes and prevent reactor fouling. Formation of uniform polymer particles with narrow size distribution and high bulk density can be expected as for conventional catalysts.

In the development of supported catalysts, virtually all types of inorganic and organic solid compound have been examined. The nature of the support and the technique used for supporting the metallocene have a crucial influence on the catalysts' performance. Inorganic oxides, finely divided polymers and other high-surface-area materials have been used as supports. The main inorganic supports used are silica, alumina and magnesium compounds. Nevertheless, less common materials such as cyclodextrine, clay minerals, polystyrene, polysiloxane derivatives and zeolities have also been investigated. Surface modification (e.g. calcination, silylation or treatment with metal alkyds such as aluminium alkyds) of the support can also be applied to influence the catalyst's properties.

It is beyond the scope of this article to give a detailed view of the different techniques for supporting metallocenes. The interested reader may find further information in the references[28] and the "further reading" section.

As a result of about 20 years of research in this area one can conclude that it is possible to support MAO activated metallocenes without losing the desired properties of the polymer. The catalysts obtained do not show reactor fouling and yield a good polymer morphology. The amount of the cocatalyst MAO that is needed could be reduced from some thousand to some hundred equivalents excess relating to metallocene, by supporting the catalyst system. Many supports give active polymerization catalysts, but silica seems to be the best suited support for metallocenes. Although the supported metallocene catalysts have been applied to industrial scale production already[29] and many research groups in industry and academia have made a great effort to find out more about the way the metallocene is bound to the surfaces most details still remain a mystery.

In addition to the MAO activated metallocenes, progress has been made to synthesize boron activated supported metallocenes too. There has been less research activity in this field up to now and most of the work done has been published in patents with only limited exceptions.[30] Heterogeneous metallocene catalysts of this type have been used in industry only recently.[31]

It seems that every producer of metallocene-based polyolefins has his own method of supporting fitted to the process used. In any case, the recipe of supporting is the best kept secret of any manufacturer, as this is the basic know-how of the catalyst's synthesis.

The crucial point in all of the syntheses is the homogeneous distribution of the catalytically active components over the catalyst particle. That way the highest activity can be achieved. The homogeneous distribution is also related to the amount of troublesome catalyst residues in films made from this polymer. In the heterogeneous polymerization processes, the carrier serves as a matrix for the polymer. The carrier is broken up during the polymerization by the growing polymer chains leaving behind only extremely small particles that will not influence the film properties. Therefore, it is extremely important to obtain a catalyst where the compounds active in the polymerization (catalyst (metallocene) and cocatalyst (MAO or boron compound)) are evenly distributed and not only sit on the outside of the carrier. Figure 15 shows an example of a catalyst where the important molecules (here: zirconocene and boron co-catalyst) are homogeneously distributed as proved by wavelength dispersive X-ray analysis.[31]

Figure 16 gives an impression how the catalyst serves as a matrix for the polymer. In this case a spherical silica has been used as the carrier and spherical polymer particles derive from them. It was not obvious to retain the carrier's structure; quite a lot of work in the catalyst development had to been done before this goal was achieved. The appearance of uniform polymer particles comes along with a high bulk density of the polymer which yields in higher output of the production plant.

After successful testing in the laboratory and promising runs in pilot plant reactors the new technology is now ready for scaling up to production plant scale.

Application of metallocene catalyst to production plant scale

A major obstacle for metallocene catalysts on their way to production plant scale was the availability of the metallocene itself and MAO. Especially MAO was not commercially available in the early stages and very expensive. In the early 1990s that obstacle was overcome and MAO was available from several suppliers (e.g. Witco, Albemarle, Akzo Nobel) but still was very expensive. By that time the chemical industry was also able to supply the metallocenes that polyolefin manufactures were asking for.

In 1991 Exxon Chemical was the first company to introduce commercially-made metallocene polyethylene to the public. They used their Exxpol catalyst technology to produce Exact plastomers in a high-pressure autoclave reactor. The products made have a density between 0.87 and 0.915 g/cm^3 and a molecular weight (M_w) of 40,000 to 120,000 g/mol. These plastomers are ethylene-alpha-olefin copolymers. As comonomers both butane and hexane have been used though most commercial grades are butane copolymers.

As mentioned above, this polymerization technology is a homogeneous process and does not require the use of supported catalysts.

Shortly after Exxon, Dow Chemical was able to commercialize ethylene-octane copolymers from their solution process in 1993. The catalyst used is of the "constrained geometry" type (*vide supra*); the whole process is call INSITE technology. The Dow metallocene polymers are known as Engage (elastomers, density below 0.90 g/cm^3) and Affinity (plastomers, density between 0.90 and 0.915 g/cm^3). These polymers have an octane content of up to 20 per cent (by weight)—much more than was possible before. Compared with standard polymers and the Exact grades they show a different (better) processability. Dow claims that this special property is caused by long chain branching, obtainable by incorporating alpha-olefins of 10-20 carbon atoms made by the catalyst itself.

Here again a homogeneous process is used for the polymerization.

In 1995 BASF introduced the first family of metallocene polyethylene from a heterogeneous polymerization process. The Luflexen family (ethylene-butane plastomers with densities from 0.903 to 0.917 g/cm^3) is made in a slurry-loop process. The supported catalyst does not leach and no reactor fouling is observed during the polymerization.

Finally, in 1995 Mitsui Petrochemical was successful in introducing metallocene catalysts to a fluidized bed reactor. As in the slurry phase, a supported catalyst has to be used. The ethylene-hexane copolymer is sold under the trade name Evolue. Mobil Chemical also reported successful runs in a fluidised bed reactor at the same time, but the product has not been commercialized yet.

In isotactic polypropylene the progress was much slower. Nearly at the same time in 1995, Exxon and Hoechst both announced commercial-scale production of m-PP. Exxon's brand name is Achieve while Hoechst named their product Hostacene. Shortly after these first announcements BASF was also able to obtain larger quantities of m-PP (brand name: Novolen M). It is expected that the German companies will speed up in their development after the formation of their joint venture Targor in mid-1997.

Meanwhile metallocene catalysts have also been used in the production of EPDM (ethylene propylene diene monomer rubber) by DSM and DuPont Dow Elastomers.

Properties of metallocene based polymers

Oligomers

Although not really polymers, this class of new compounds offers access to a large variety of molecules and will therefore be mentioned briefly.

Unlike Ziegler/Natta catalysts metallocenes form a high degree of unsaturated double bonds when the polymerization terminates. This reactive double bond may be further functionalized to yield a virtually unlimited number of molecules that might be used in other chemical processes or several end-user applications. Figure 17 shows some typical examples.

While Phillips (chromium) catalysts also provide polymers and oligomers with a terminal double bond, they lack the property of producing uniform polymers. With metallocene catalysts it is possible to obtain uniform oligomers (narrow molecular weight distribution) with a terminal double bond. To get such oligomers instead of polymers very bulky metallocenes with large substituents at the cp-ring are used. Especially propylene has been shown to be very useful in this regard. Still, no products based on these oligomers have been commercialized yet.

Polyethylene

Conventional catalysts such as Phillips and Ziegler/Natta catalysts always consist of a mixture of different active sites. As illustrated in figure 18 some catalytic centres typically produce short polymer chains and incorporate quite large amounts of comonomer while others produce very high molecular weight polymers with nearly no comonomer incorporated. Thus, conventional catalysts give polymers that are not uniform in two ways: (1) they have a broad molecular weight distribution; and (2) they show a heterogeneous comonomer distribution (comonomer in the low molecular weight part and nearly no comonomer in the high molecular weight part).

In contrast, metallocenes can be described as single site catalysts. The exact nature of the catalytic centre's environment, determined by the cyclopentadienyl ligand framework, assures that only one type of active centre is formed. Therefore, only one type of polymer can be produced. Consequently, metallocene-based polymers show both narrow molecular weight and comonomer distribution.

The molecular weight of the polyolefins is generally determined by gel permeation chromatography (GPC). This method is a special type of size exclusion chromatography, where the larger (higher molecular weight) particles do not fit into the pores of the carrier material and are eluted first from the column. Smaller particles may diffuse into the pores and are eluted later.

The comonomer distribution of a polyethylene can be determined by TREF (temperature rising elution fractionation). Here the polymer is fractionated by crystallinity (density). The polymer fraction with the highest amount of comonomer (lowest density) is dissolved first at low temperatures. Polymers with low amounts of comonomer (high density) will not dissolve until higher temperatures of the solvent are applied. Typical TREF plots (figure 19) therefore show amount of polymer eluted versus temperature. As can be seen, the metallocene polymer shows a much narrower comonomer distribution than the conventional polymer.

A combination of the two methods (cross-fractionation) can be applied to find out, whether the comonomer is incorporated in chains of all lengths or if certain molecular weights are preferred. From figure 20 it is obvious that metallocenes yield a much more uniform polymer than standard catalysts.

From the application point of view it is desirable to have a polymer with a broad molecular weight distribution but with more comonomer in the high molecular weight part than in the low molecular weight part. This is impossible to obtain with conventional catalysts using one reactor. Only the use of cascade technologies allows the access to such polymers nowadays. Metallocenes allow the production of such a polymer with a so-called inverse comonomer distribution by combining two metallocenes, one that produces high molecular weight polymers with large amounts of comonomer and one producing low molecular weight chains with only small amounts of comonomer. A calculated GPC and comonomer distribution curve is shown in figure 21.

The influence of these new polymer properties on product performance will be described in the next section.

Polypropylene

Metallocene catalysed isotactic polypropylenes differ from their Ziegler/Natta analogues by a narrower molecular weight distribution. In addition, it is possible to influence the melting point of the polypropylene by varying the degree of mis-insertions of the propylene molecule as described above (figure 6). If a propylene molecule is not inserted in the regular 1-2 but 2-1 fashion the crystallinity of the isotactic polypropylene is disturbed. A lower melting point is the consequence. It is therefore possible to obtain lower melting polypropylene without losing its overall properties.

As described for polyethylene, the comonomer (e.g. butane) incorporation is homogeneous for polypropylene, too.

Another important feature of metallocene catalysts is that they are more sensitive to hydrogen to lower the molecular weight than Ziegler/Natta catalysts. Until now very low molecular weight polypropylenes that, for example, are required for some special injection moulding applications had to be made by degradation with peroxides causing problems with increased yellowness, odour and oligomers. Additionally, extremely low molecular weight polymers used in melt blown fabrics—a special fibre application—are only accessible via metallocenes.

Advantages of metallocene-based polymers

Polyethylene

The major difference of metallocene polyethylene compared with conventional polyethylene is the crystallization behaviour. Due to the homogeneity of the polymer it crystallizes very well and shows a uniform distribution of crystalline and amorphous regions. The thickness of the lamellae (formed by cocrystallization of the comonomer poor parts of the chains) is homogeneous and rather small.

In contrast, conventional polyethylene shows a heterogeneous picture. Here the high molecular weight chains without any comonomer form thick lamellae while the short chains with a lot of comonomer fill the gaps in between but are not able to participate in cocrystallization in any lamellae (see figure 22).

The observed facts result in a variety of product improvements:

1. **Lower melting point**

The melting point is mainly determined by the thickness of the lamellae. Due to the lack of high molecular weight chains without any comonomer in metallocene polyethylene, thick lamellae (large crystalline areas) cannot be formed. Less energy is required to melt the (rather thin) lamellae and the melting point is lowered.

The low melting point affects the sealing properties of the polymers. This property is important whenever films (e.g. for packaging) have to be attached to each other.

2. **Low crystallization point**

The fact that the metallocene polyethylenes show only small crystallites also results in an improvement of the optical properties. These crystallites are so small that they cannot be seen by the human eye. Therefore, the transparency and gloss is improved. In addition, the low crystallization point results in an excellent flexibility even at very low temperatures.

3. **Low extractables**

As mentioned above, metallocenes produce polymers with a narrow molecular weight distribution. This, and the fact that the low molecular weight fraction of the polymer does not contain extremely large amounts of comonomer, results in a very low content of extractable polymers. If they are in the polymer they can influence the organoleptic properties (odour, taste). With the new metallocene polyethylenes, it is now possible to increase the penetration of markets where organoleptics play an important role (e.g. food and medical sector).

4. **Improved mechanical properties**

Due to the properties of the homogeneous comonomer and narrow molecular weight distribution the chains (so-called tie molecules) connect the crystalline and amorphous parts of the polymer very well. It is therefore difficult to tear the different areas apart. Thus improved mechanical properties arise.

Besides the great advantages of metallocene polyethylene, it is necessary to mention one disadvantage. The narrow molecular weight distribution causes lower shear sensitivity which comes along with poorer processability on standard process equipment. Still, after the first years of using metallocene polymers, polyethylene manufacturers and processors have developed methods to process the new materials.

The described polymer properties have resulted in a variety of product improvements. Although the market for these new resins is still developing, some areas have been identified where the new polymers have made the largest impact.

Films produced with the new polymers show much better mechanical properties as well as extremely good optical performance. Especially worth mentioning is the performance in dart drop. Here the values obtained are much higher than can be measured with standard polymers. Figure 23 lists film properties of metallocene polyethylene in comparison with conventional polyethylene. Figure 24 shows the performance of Luflexen 0322 H.

For several film applications the whole potential of metallocene polyethylene is not needed, and blends with other polymers such as LDPE already give resins with improved properties.

Another area where the new material has shown its outstanding performance is in the field of injection moulding. Here the low-temperature properties are greatly enhanced due to a much more flexible behaviour. Major products are household containers for freezer storage.

These are just are few applications and it is expected that the variety of uses will increase with the number of processors that are examining metallocene polyethylenes.

Polypropylene

So far, metallocene polypropylene faces applications in injection moulding, fibre spinning and BOPP (biaxially orientated polypropylene) films.

In injection moulding the homopoylmers have the advantage of responding much better to nucleating reagents than Ziegler/Natta polymers, yielding hitherto unattainable levels of transparency in PP homopolymers.[32] An even better transparency of 96 per cent (the highest value seen in any polypropylene to date) can be achieved by using metallocene random copolymers. These polymers can be used in household articles, thin-wall packaging and transparent drinking cups where good visibility is required. Here again, the narrow molecular weight distribution causes very low extractables and favours their use in food applications.

Summing up, the advantages of metallocene-based polypropylene in injection moulding are: (1) higher clarity/transparency; (2) higher stiffness; and (3) reduced cycle times leading to higher output.

In fibre applications, metallocene-based polypropylene shows the following advantages: (1) finer filaments; (2) higher toughness; (3) less volatile; (4) higher throughput; and (5) higher drawability.[33]

Metallocene homopolypropylene combines a reduced melting point with good stiffness and excellent optical properties. Thanks to narrow relaxation time spectra and an enhanced number of tie-molecules, it provides better performance when stretched in the partly molten state. Thus, it is superior to existing grades in some large volume applications, such as BOPP-film production and fibre spinning, offering a very attractive market potential.[34]

Major industrial players and polymers commercialized already

Polyethylene

In the market of metallocene-based polyethylene, the companies that started the race still remain the top runners.

Exxon Chemical has extended the Exact plastomer product line by the Exceed family, a linear low-density polyethylene (LLDPE) made in a fluidized bed gas-phase reactor targeting film applications. Exxon has brought the metallocene activities into a joint venture with Union Carbide (Univation) in 1996. This new joint venture is expected to concentrate on developments in the gas-phase and the licensing business. In addition, Exxon has formed a joint venture with DSM to produce plastomers in a solution process. No product has been released yet. In Japan, Exxon is cooperating with Mitsubishi Chemical in the field of high-pressure polymerization.

Dow Chemical has also added a new class of polyethylenes to its portfolio. *Elite* polymers are also LLDPE and target the same market as the Exceed grades. To develop a metallocene catalyst for gas-phase processes, Dow started an alliance with BP Chemicals in 1996. With regard to the production of EPDM Dow has formed a joint venture with DuPont (Du Pont Dow Elastomers).

BASF is producing Luflexen in the slurry loop process but is also developing a catalyst for the gas-phase process.

Besides the first trial runs, nothing more has been heard about Mobil Chemical's activities. This silence is probably caused by patent disputes.

To avoid these disputes, Borealis has taken a licence from Exxon and is now producing medium-density grades specially for rotomoulding applications in a slurry loop reactor.[35]

Mitsui Petrochemical cooperates with Sumitomo and Ube in gas phase polymerization. The LLDPE polymers are marketed under the brand name Evolue. In addition, Mitsui Petrochemical is involved in producing plastomers in a solution process.

Very recently, Phillips Chemical announced successful runs of metallocene polyethylene in a commercial-scale slurry loop reactor.

To summarize, it can be concluded that at this time only four companies have fully commercialized metallocene polyethylene: Exxon, Dow, BASF and Mitsui Petrochemical. Yet other players are entering the game and are increasing the competition.

Polypropylene

As already mentioned above, the development of metallocene-based isotactic polypropylene has been slower than in the polyethylene field. The products that are commercialized so far include both Hostacen and Novolen M from Targor (the BASF/Hoechst polypropylen joint venture) and Achieve from Exxon.

Outlook

It is very difficult to project the future of metallocene-based polymers, since market penetration has been somewhat slower than expected. The potential market for metallocene polyethylene is seen somewhere between 1.5 and 8 million tons worldwide, whereas estimates for polypropylene are in the range of 0.5 to 1.8 million tons worldwide in the year 2000. These differing projections make it very hard to plan the addition of new capacity or adaptation of existing plants. Anyway, the new polymers will find their markets because in target applications their properties are much better than the ones of existing grades. The possibility to mix two or more metallocene catalysts will result in additional new polymers with exceptional properties. The overall question will be if the market is willing to pay a higher price for these advanced resins.

A major concern in the metallocene business is still the patent situation. It seems that the patent rights are fairly fragmented among the major players and it might be difficult for some companies to get the freedom to operate. Therefore, it is believed that only a handful of global players will rule the metallocene business while others will licence in.

Even though metallocene polymers have been known for quite some time, the number of patents filed has skyrocketed in the last few years; yet there is no limit visible (see figure 25). Metallocene catalysis still remains an active area of industrial and academic research.

Effect on developing countries

As has been mentioned above, metallocene polymers show an excellent performance in a variety of applications. Most important is the increased toughness and mechanical strength. This property can either lead to improved products or it can be used to reduce the amount of polymer needed to manufacture a part. By the reduced amount of polymer needed (down-gauging) a lot of material can be saved. This might have an impact on the overall consumption of oil (since ethylene and propylene are partially made from naphtha).

More important, metallocenes offer not only improved but also new properties. An important application in developing countries might be the use of breatheable packaging for prepared produce. It has been shown[36] that vegetables that are packed in films of metallocene polyethylene stay fresher for a much longer time than if they were packed in ordinary films. This could result in a better food supply, since shipping problems caused by spoiling are reduced.

Here again, the market for metallocene polymers has just started to grow and one never knows how much impact further applications might have on developing countries.

Finally, the new metallocene catalysts are designed to work as "drop-in catalysts". That means that these catalysts will run in any of the processes where they have been made for, regardless of its site. Whether in Europe, Africa, America or Asia the metallocene technology will be accessible worldwide.

Summary

The discovery of metallocene catalysts has led to the most dramatic changes ever seen in the polyolefin industry. A new class of polymers is available with properties never thought about before in the polyolefin business. The unique possibility to tailor the catalyst according to need makes metallocene catalysts a versatile and very valuable tool in the hands of chemists and product developers.

Although market penetration of the new resins was slower than expected by researchers, metallocene-based polymers will have a bright future. One can be curious about the next developments that will be made in this fast-growing field.

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Glossary

Cocatalyst

Compound that is needed to transform a catalyst precursor in its catalytically active form. In metallocene catalysis MAO and special boron compounds are used as cocatalysts.

Comonomer

Other monomer than the main monomer that is used. Usually the comonomer content of a polyolefin is between 0 and 20 per cent. In polyethylenes butane, hexane and octene are widely used, while comonomers in polypropylene mostly involve ethylene and butane.

Drop-in catalyst

Catalyst that can be used in existing polymerization plants without major modifications. Metallocene catalysts are designed to be drop-in catalysts.

Elastomer

Polymer with elastic properties. Polyolefins with this properties generally have densities below 0.90 g/cm^3 and a comonomer content of up to 20 per cent by weight.

GPC

Gel permeation chromatographie. Method to determine the molecular weight and the molecular weight distribution.

HDPE

High density polyethylene. Homopolyethylene or copolymer with small amounts of butene or hexene that has a density between 0.97 and 0.94 g/cm^3. HDPE for example is used in films (shopping bags) and blow moulding (fuel and oil tanks).

Isotactic polymer

Polymer made of alpha-olefins other than ethylene (e.g propylene) where the substituents of the polymer chain's back bone point all in one direction.

LDPE

Low density polyethylene that has a lot of branches produced in high pressure reactors. The major application is in films.

Ligand

General name of a chemical group that is bonded to a metal atom. The bonding can either be coordinative using neutral ligands (e.g. ammonia (NH_3) or carbon monoxide (CO)) or covalently using charged ligands (e.g. chlorine-ion (Cl^-) or cyclopentadienyl ((C_5H_5)).

LLDPE

Linear low density polyethylene. Copolymer of ethylene with butene, hexene or octene. Densities of LLDPE are normally in the range of 0.930 to 0.915 g/cm^3. LLDPE is widely used in film applications.

MAO

(Methylalumoxane) partly hydrolyzed trimethyl aluminium, that is used as cocatalyst in polymerizations with metallocenes.

Metallocene

Organometallic compound where the central metal atom is bound to at least one cyclopentadienyl ligand.

***ansa*-Metallocene**

Metallocenes where the two cyclopentadienyl units are linked by a bridging group (e.g. Me_2Si or C_2H_4).

Molecular Weight (M_w, M_n)

Important property of a polymer. It is distinguished between the weight average (M_w) and the number average (M_n). The ratio (M_w/M_n)is a means to describe the molecular weight distribution (MWD). Living polymers have an MWD of 1; metallocene polymers (ideally) 2. Polyolefins made by standard catalysts have a MWD of 4-30 and some times even higher.

Molecular Weight Distribution (MWD)

Ratio of weight average (M_w) to number average (M_n) molecular weight. Means of describing the uniformity of a polymer. Living polymers have an MWD of 1, metallocene polymers (ideally) 2. Polyolefins made by standard catalysts have a MWD of 4 - 30 and some times even higher.

Phillips catalyst

Silica supported chromium based catalyst for polyethylene production. Invented by Phillips Petroleum Company (USA).

Plastomer

In the polyolefin business polymers with densities between 0.915 and 0.90 g/cm^3 are generally referred to as plastomers.

Syndiotactic polymer

Polymer made of alpha-olefins other than ethylene (e.g propylene or styrene) where the substituents of the polymer chain's back bone are alternatingly pointing in different directions.

TREF

Temperature rising elution fractionation. Method to determine the comonomer distribution.

Ziegler/Natta Catalyst

Polymerization catalyst based on titanium and aluminium for the production of polyethylene and polypropylene. Generally used as supported catalyst with magnesium chloride or silica as the carrier. Invented by the Professors Ziegler (Germany) and Natta (Italy).

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The author is willing to enter into correspondence with interested readers. Please contact him directly:

Dr. Marc Oliver Kristen, BASF AG, Polymer Laboratory, Department of Polyolefins
ZKP/NE - M 510
67056 Ludwigshafen, Germany
Fax: +49-621-60-56574
e-mail: marc.kristen@zkp.x400.basf-ag.de

Figure 1. Metallocene structures

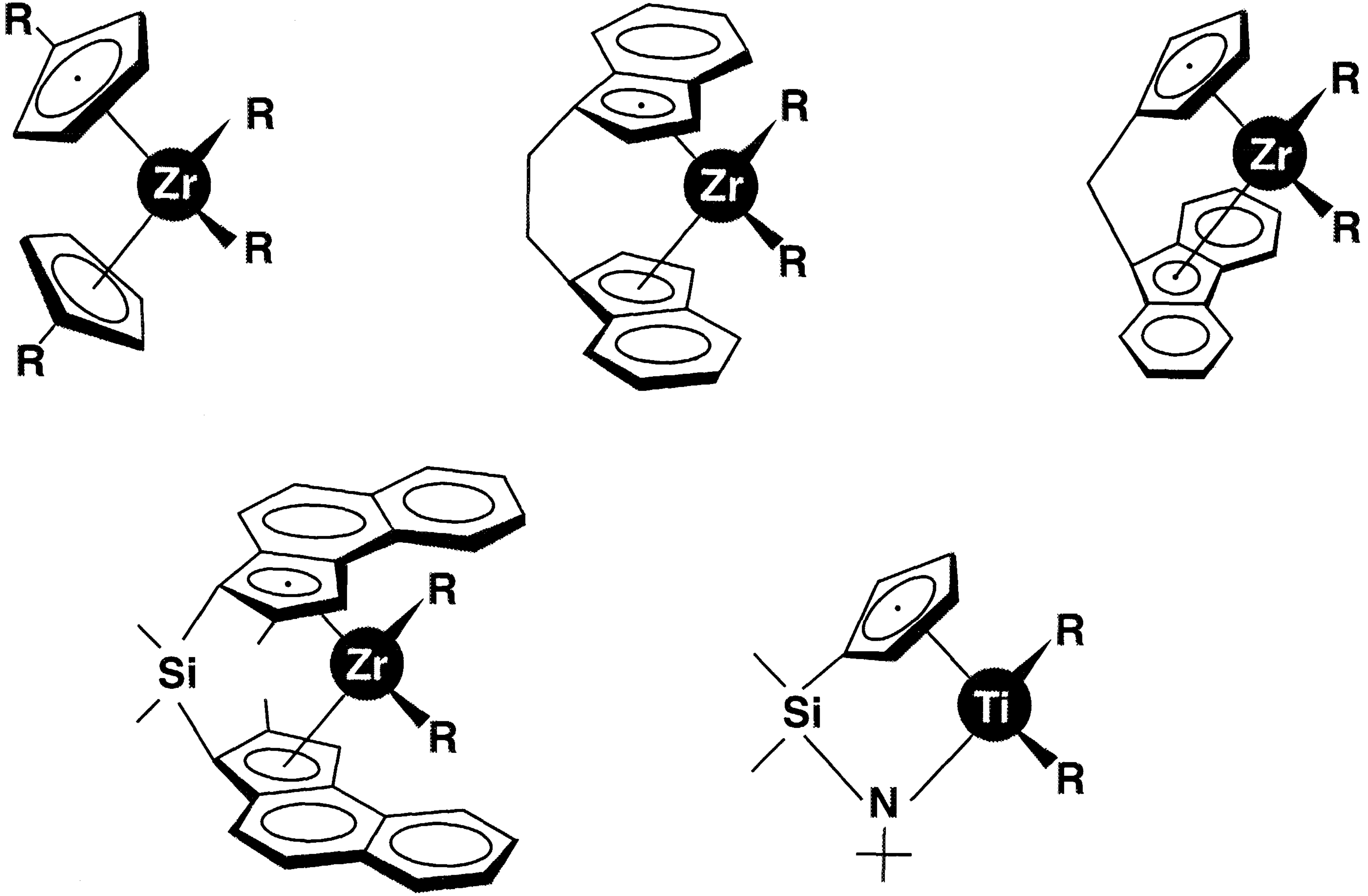


Figure 2. MAO activation of metallocenes

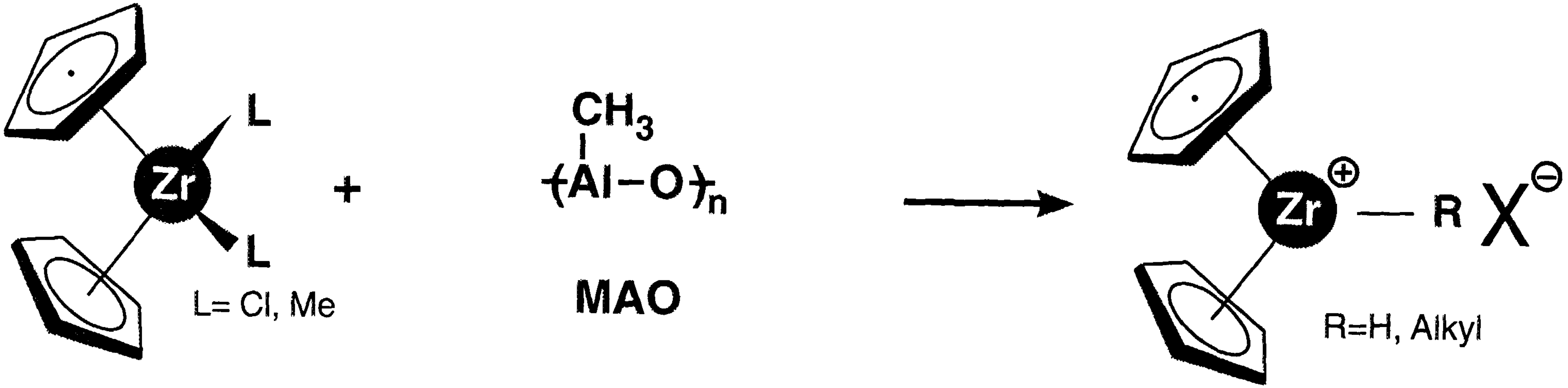


Figure 3. Boron activators for metallocenes

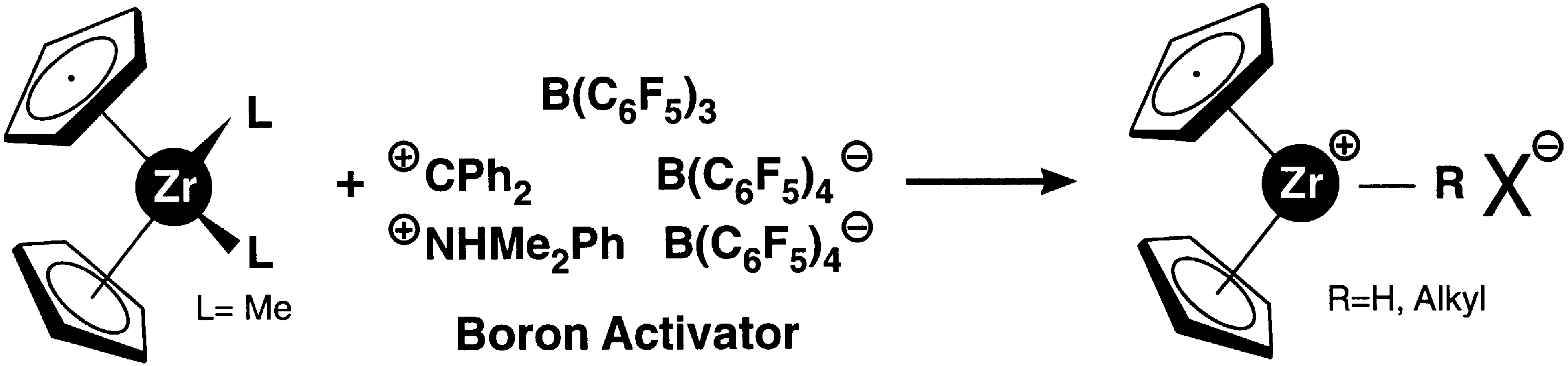


Figure 4. Control of stereoselectivity by ligand sphere

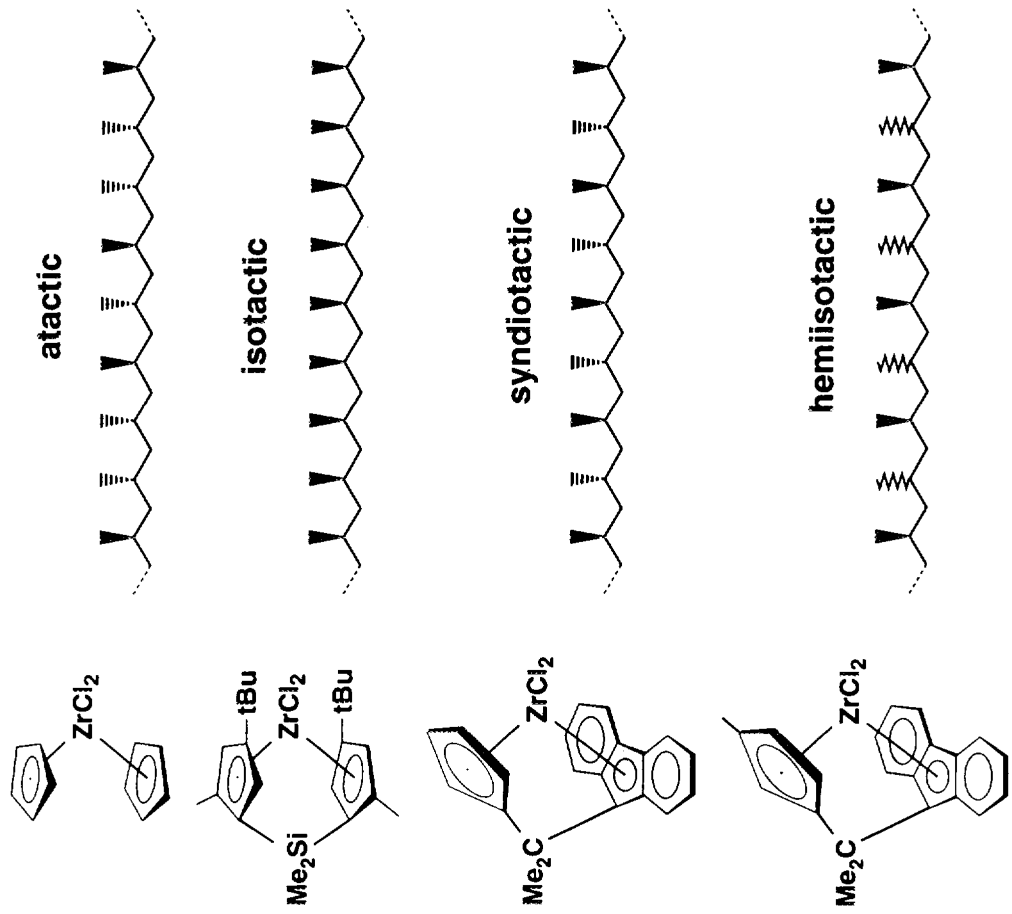
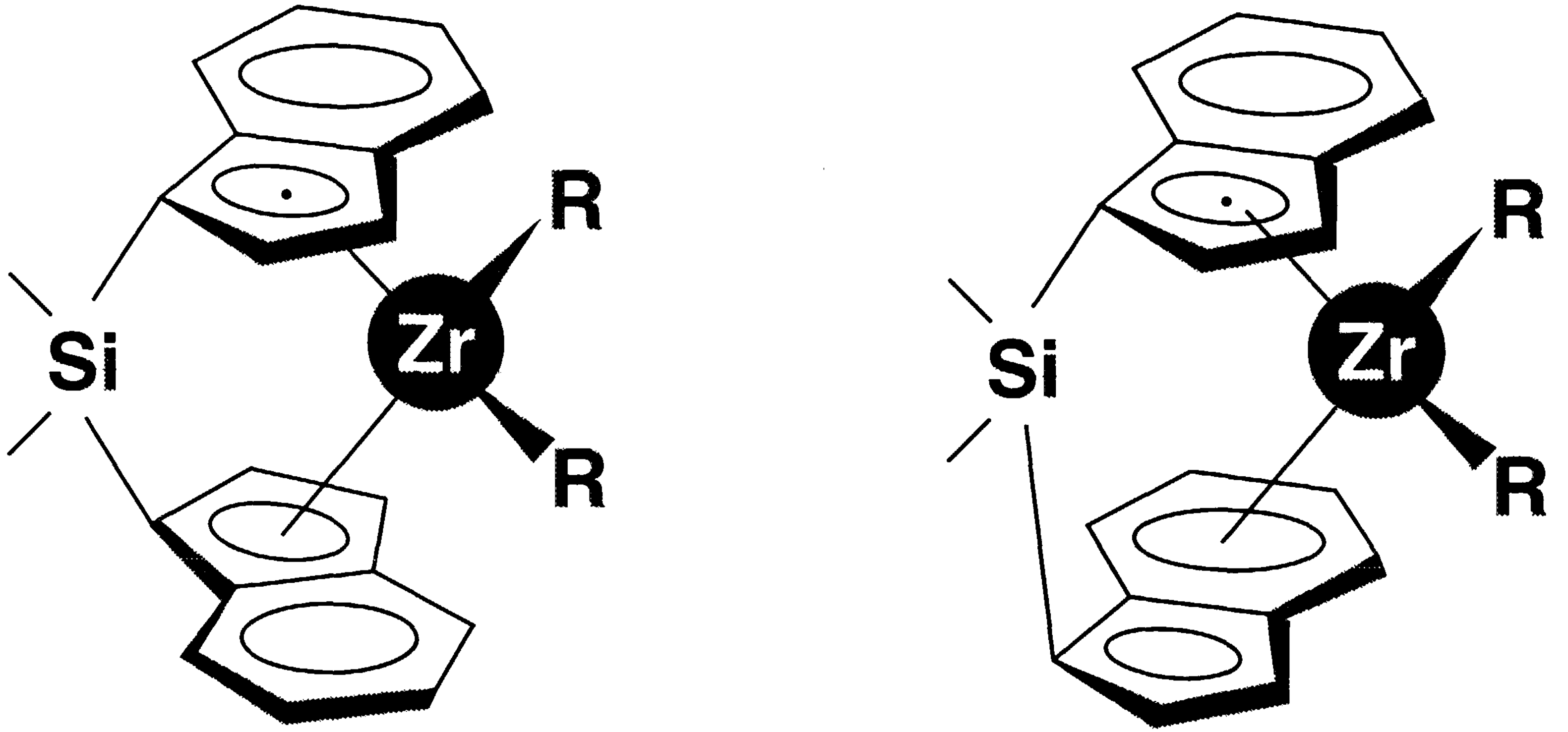


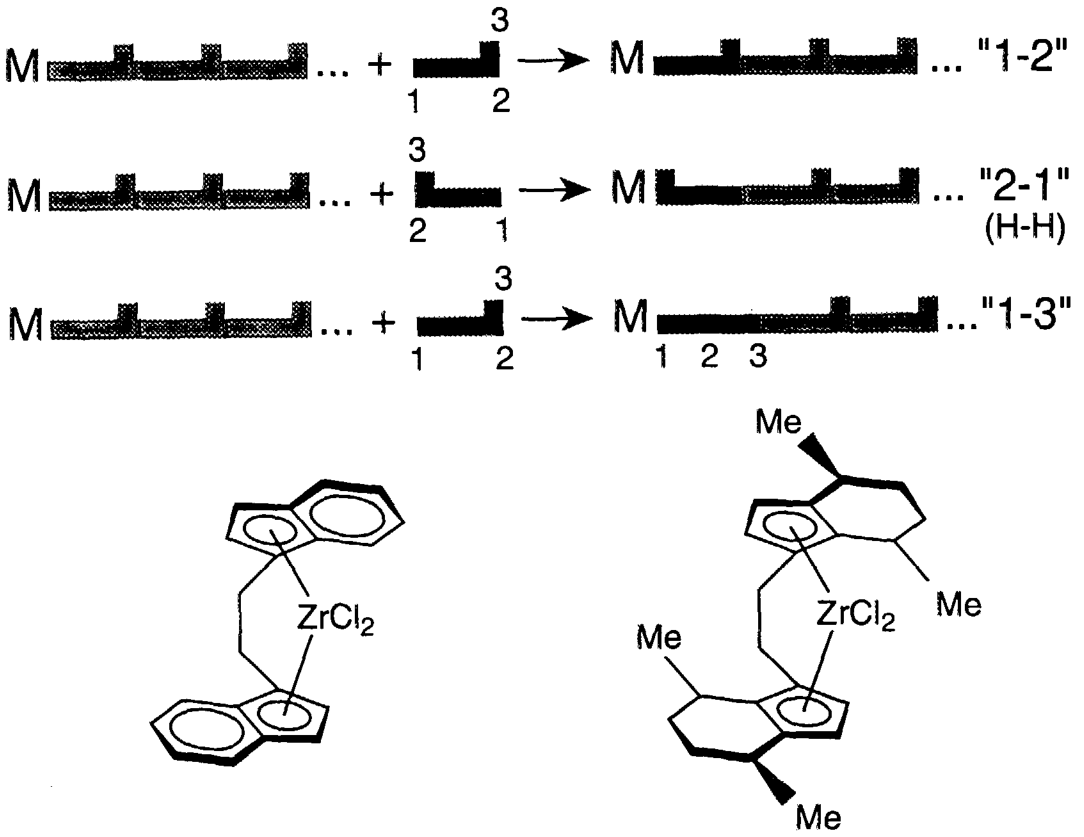
Figure 5. Rac-/meso-form of *ansa*-metallocenes



rac form

meso form

Figure 6. Control of regioselectivity



0.1% "1-3": crystalline

23.7% "1-3": amorphous

Figure 7. Control of comonomer incorporation

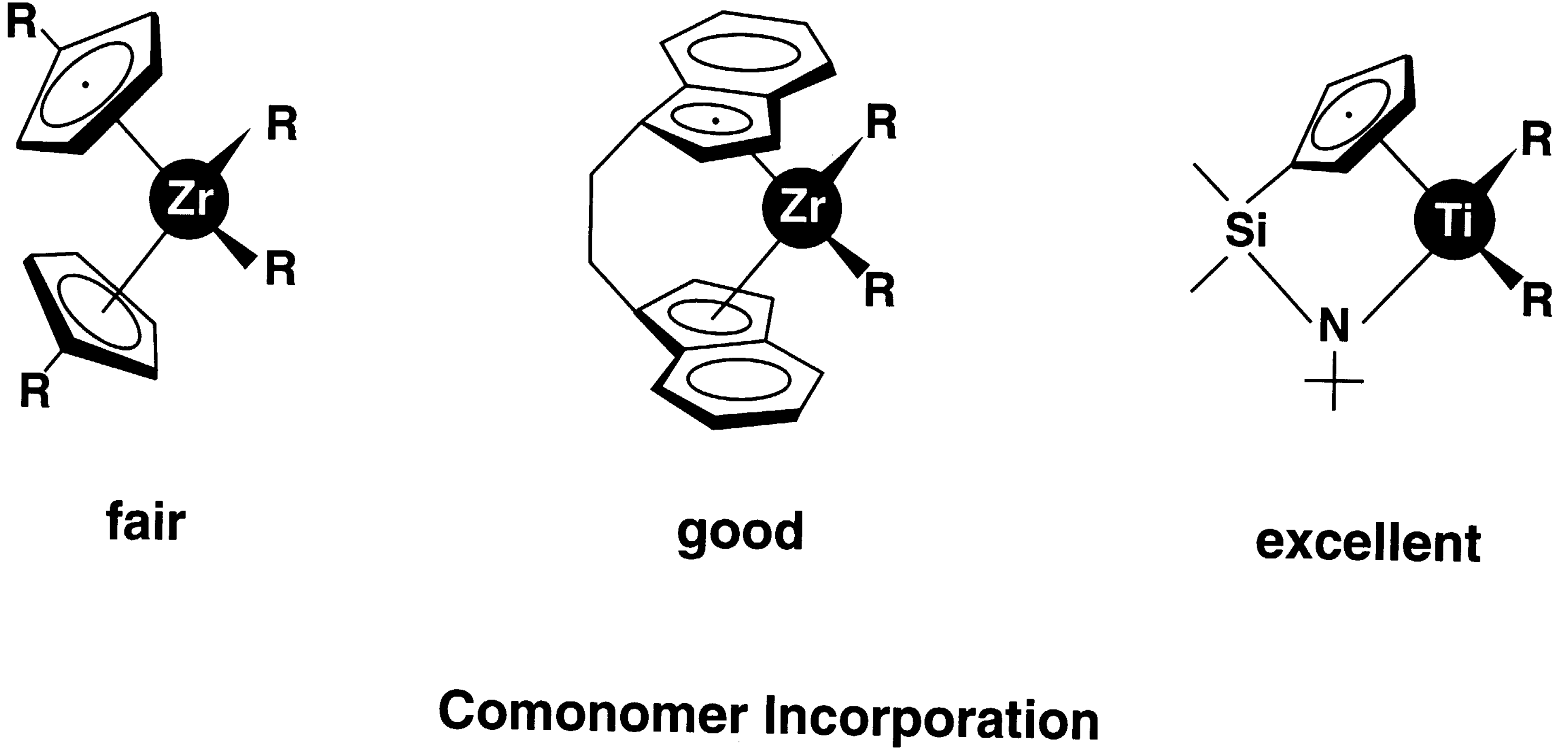


Figure 8. Control of molecular weight

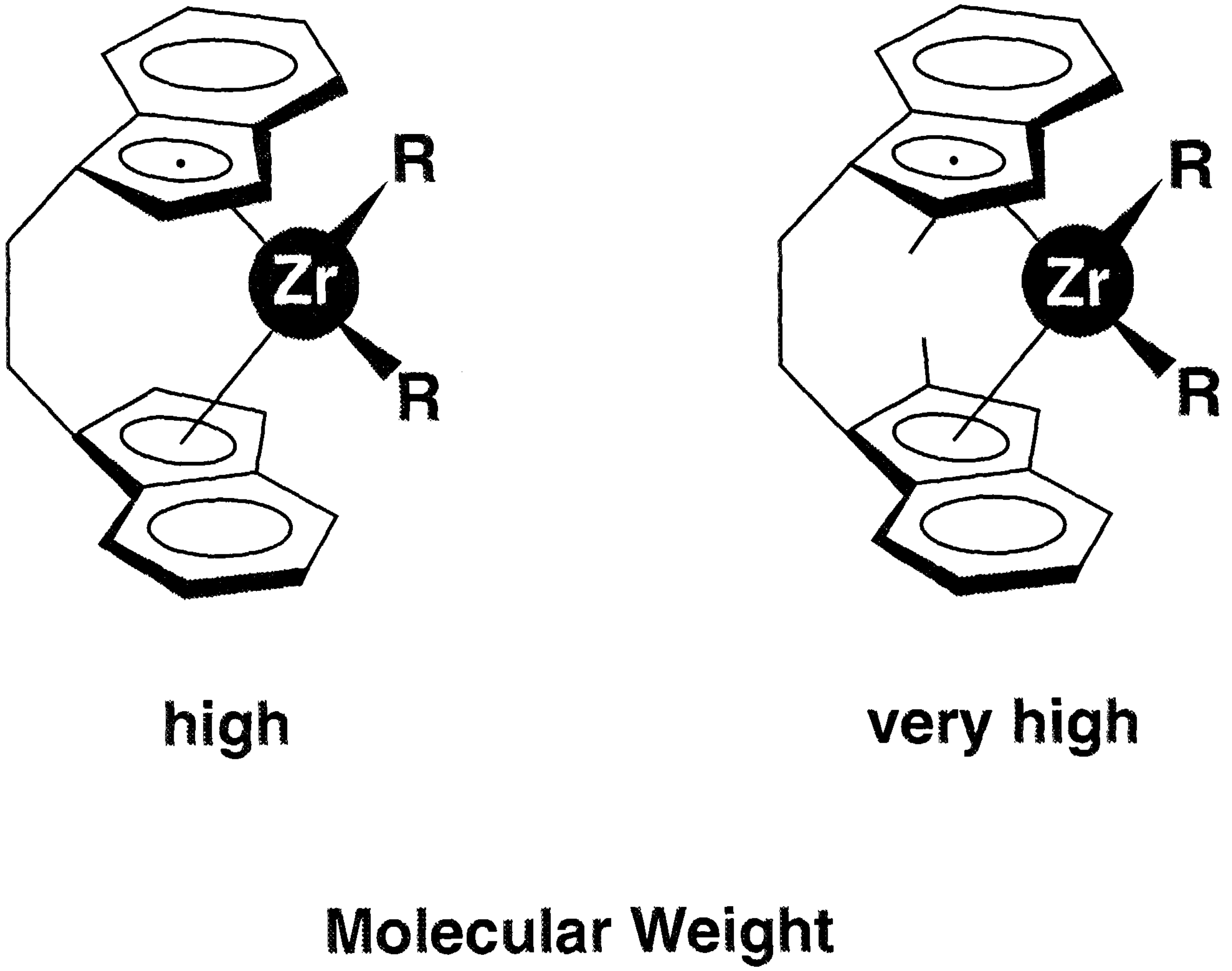


Figure 9. Control of block structure

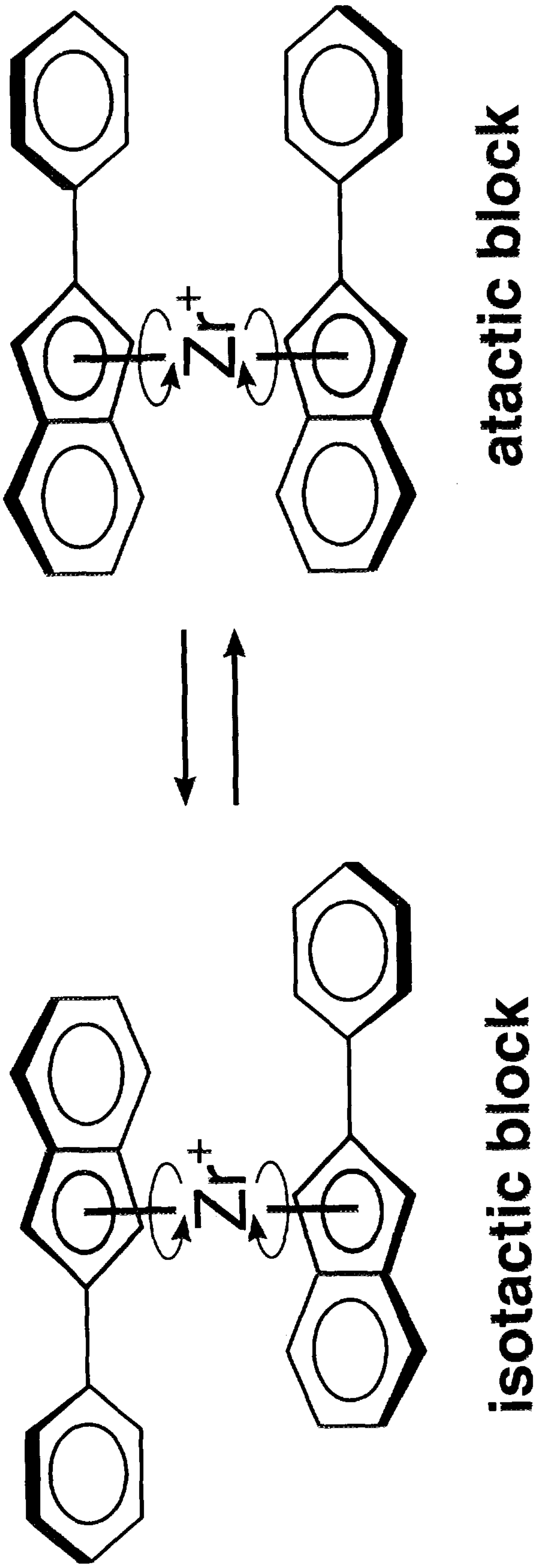


Figure 10. Syndiotactic polystyrene/poly(isocyanate)

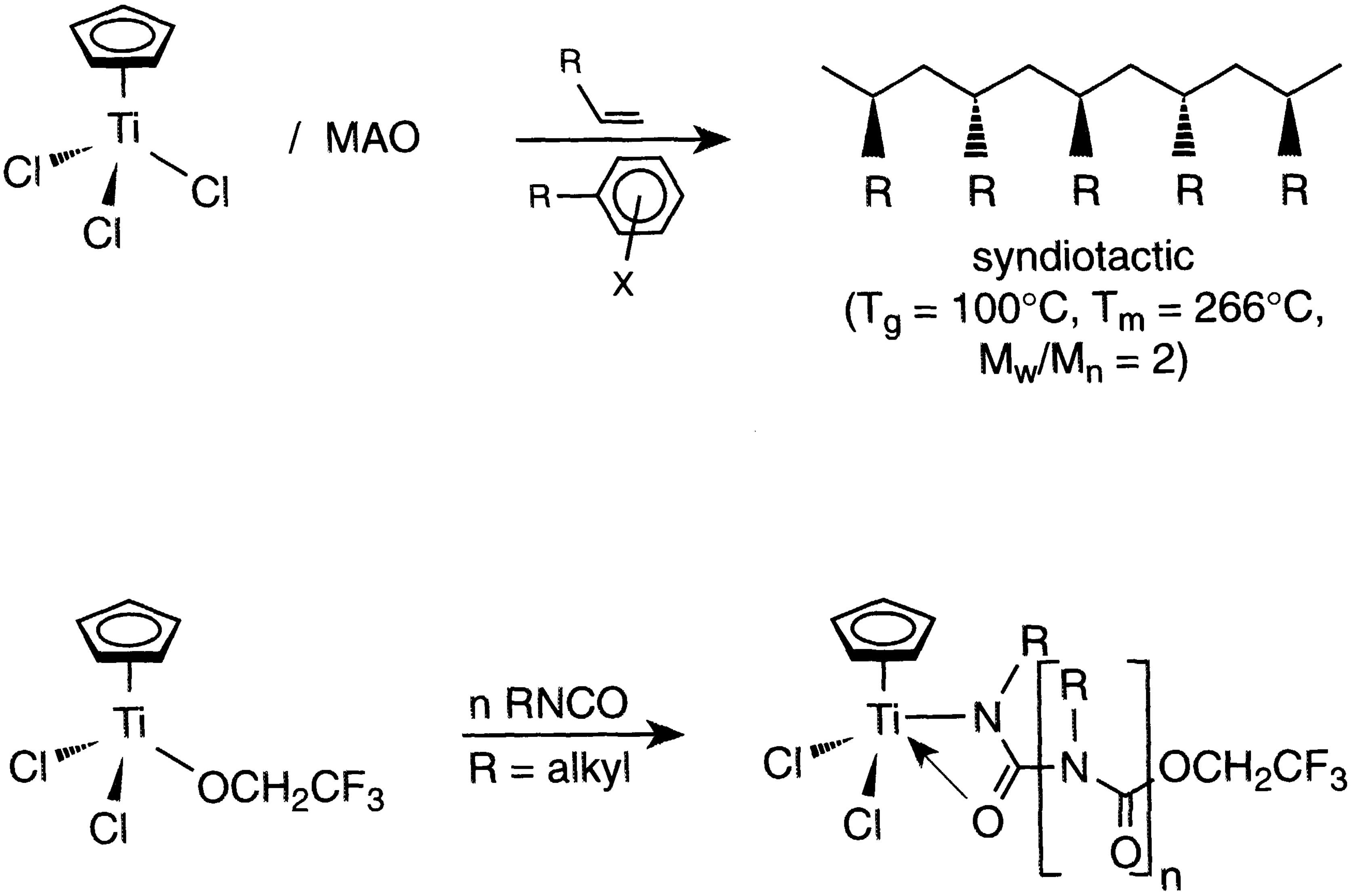
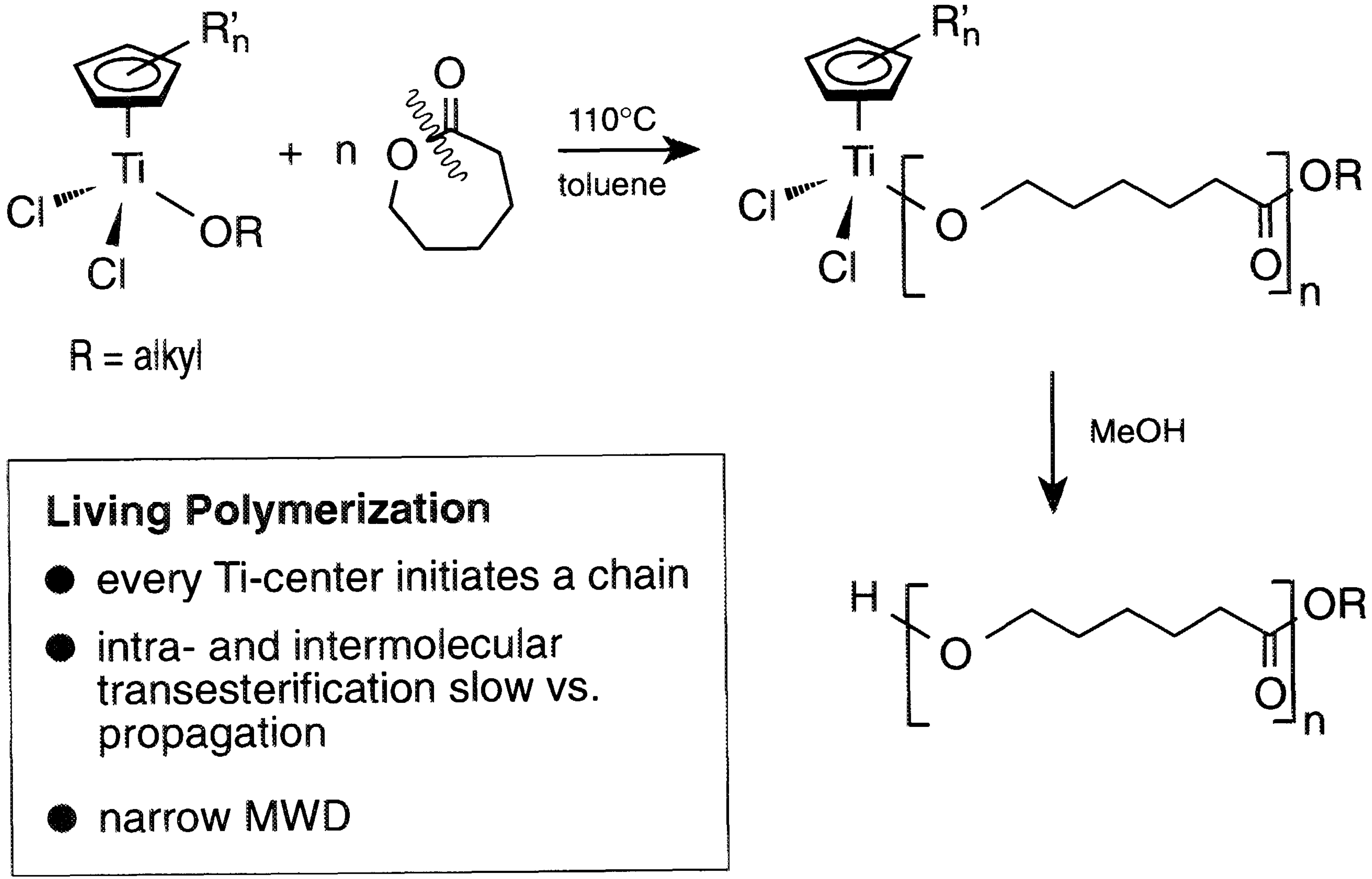


Figure 11. Ring-opening polymerization of ε-caprolactone



Living Polymerization

- every Ti-center initiates a chain
- intra- and intermolecular transesterification slow vs. propagation
- narrow MWD

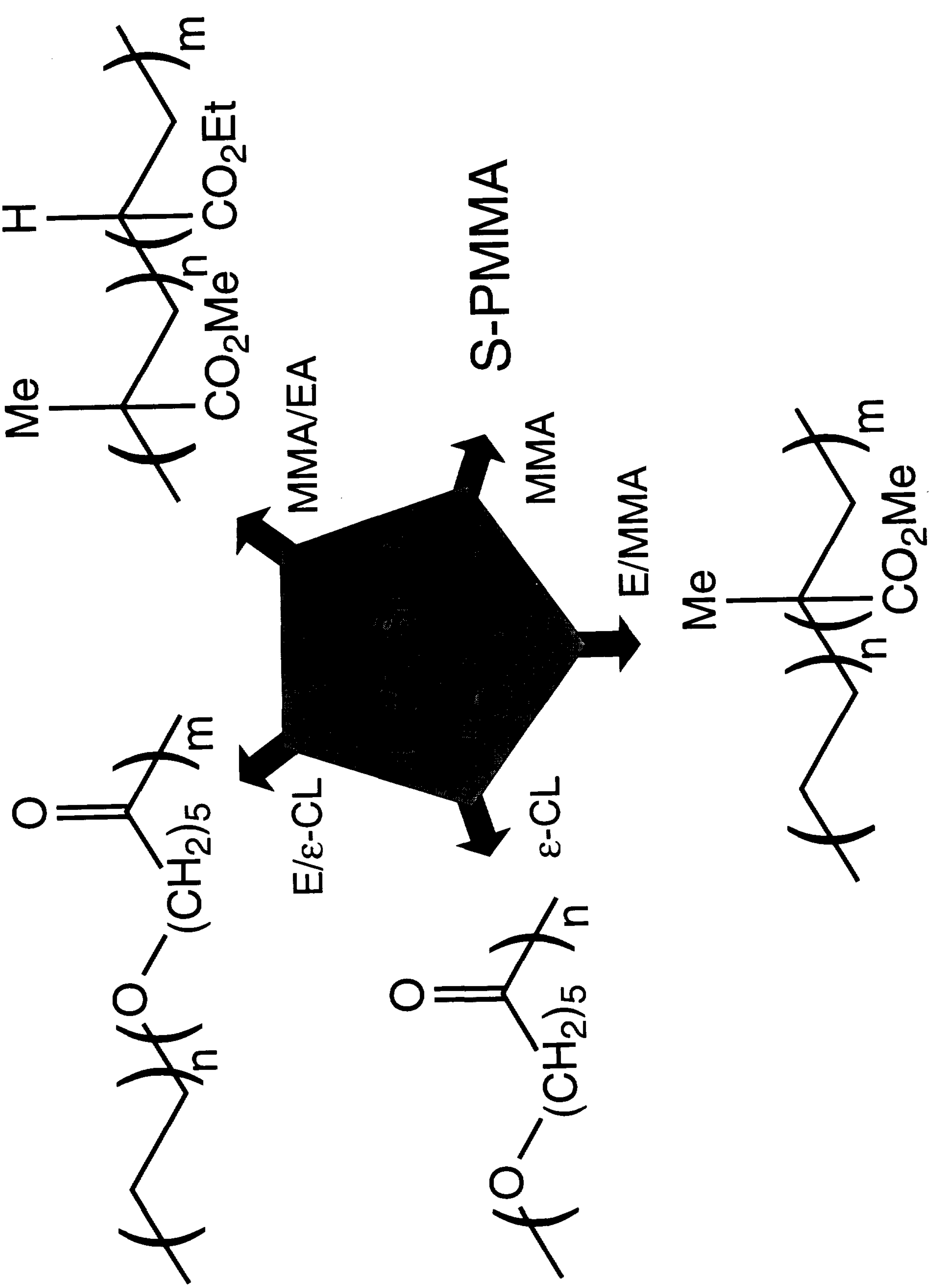
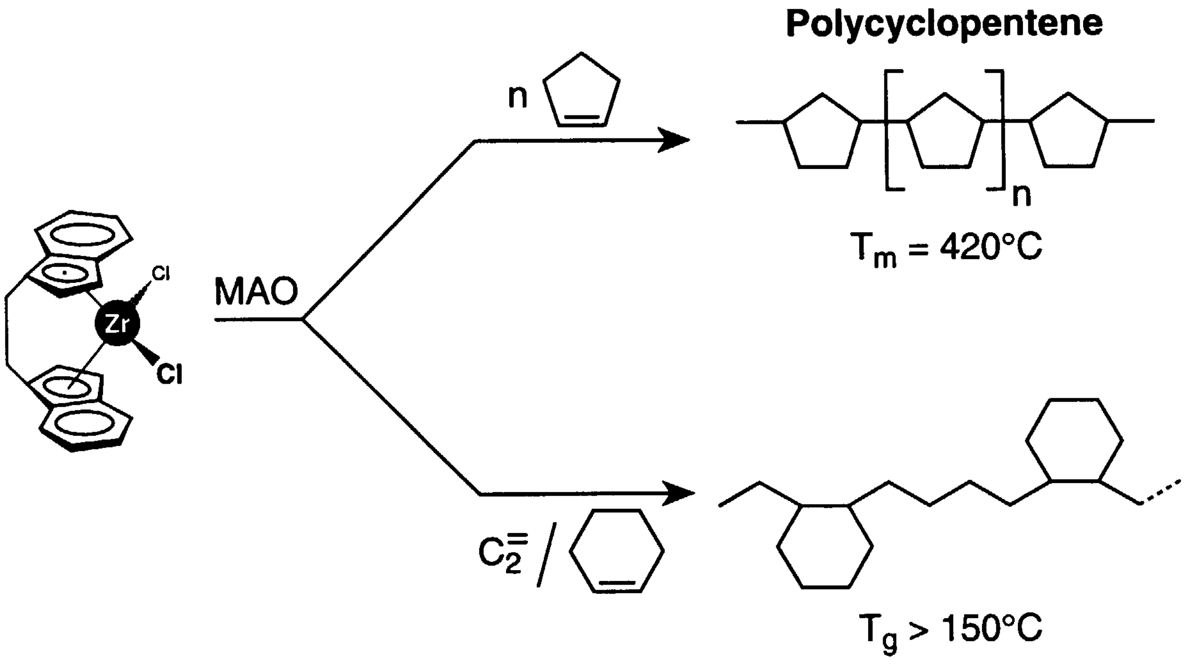


Figure 12. (Co-)polymerization of polar monomers

Figure 13. Cycloolefin homo- and copolymers



- transparent
- very low uptake of moisture
- resistant to chemicals

⇒ **optical discs**

Figure 14. Enantioselective synthesis of chiral polymers

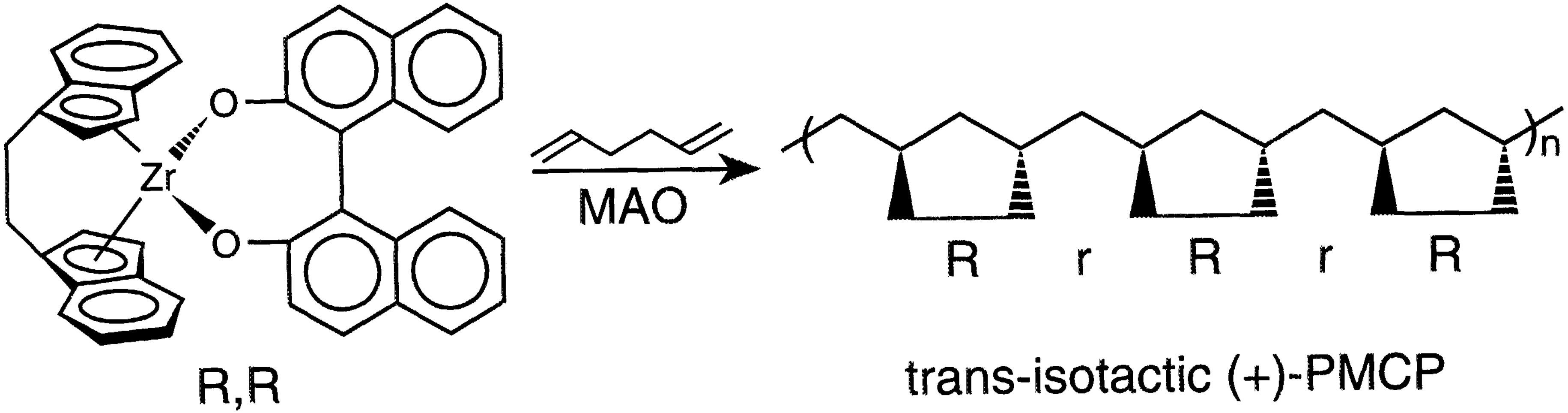


Figure 15. Homogeneous distribution of active components ©BASF

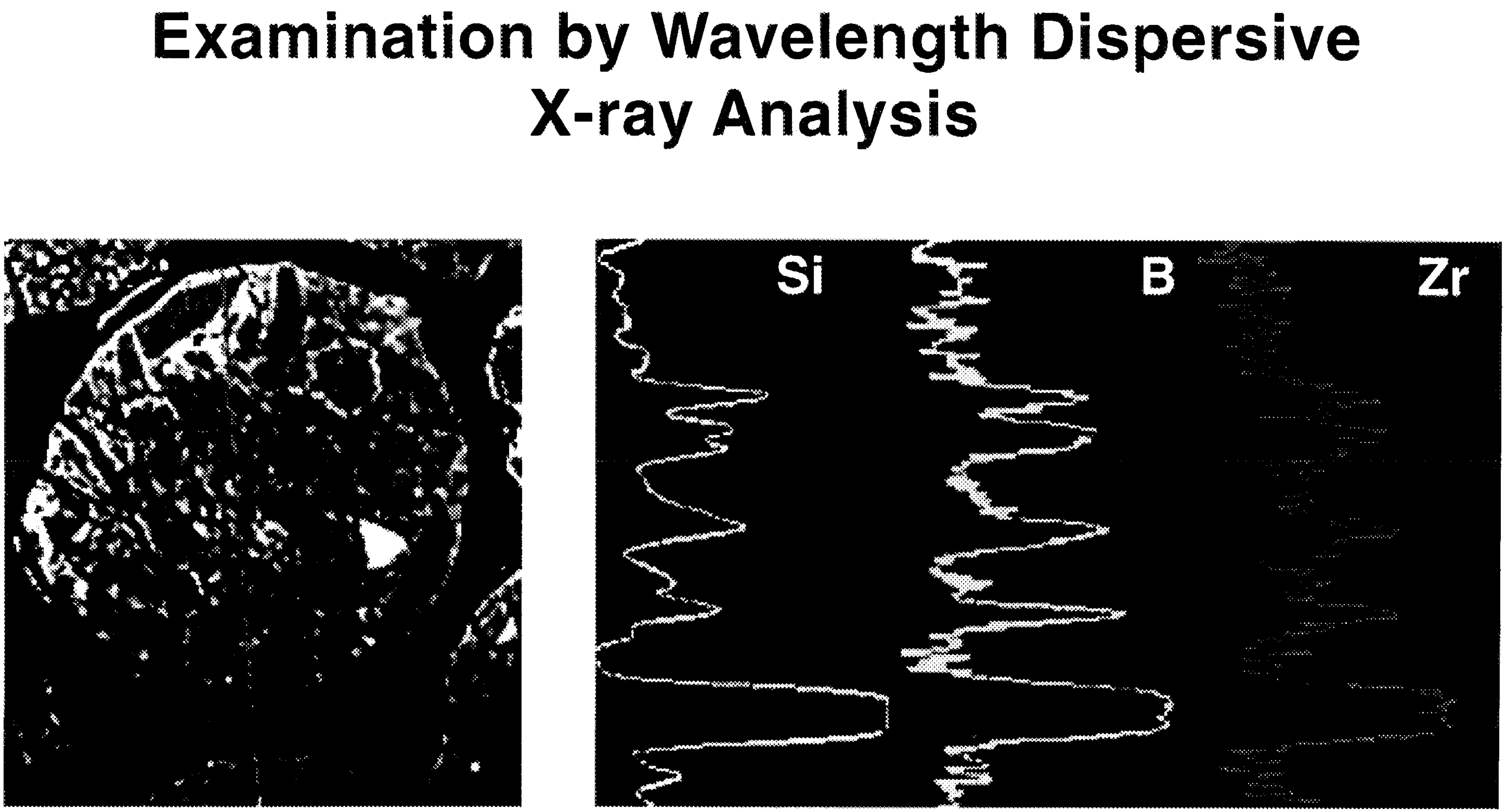
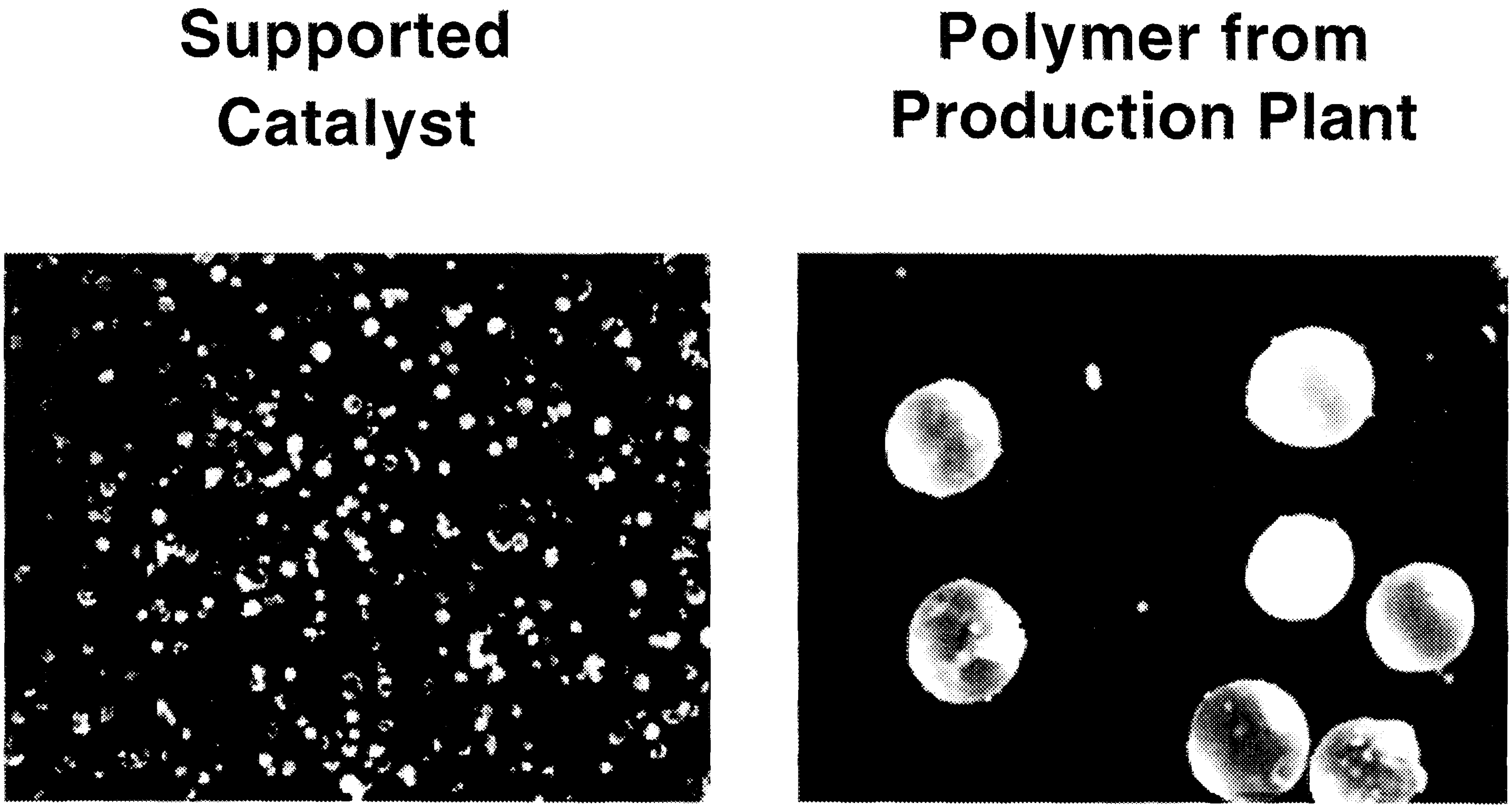

Examination by Wavelength Dispersive X-ray Analysis

Figure 16. From catalyst to polymer particles ©BASF



Supported Catalyst

Polymer from Production Plant

Figure 17. Propylene oligomers—functionalizations and applications

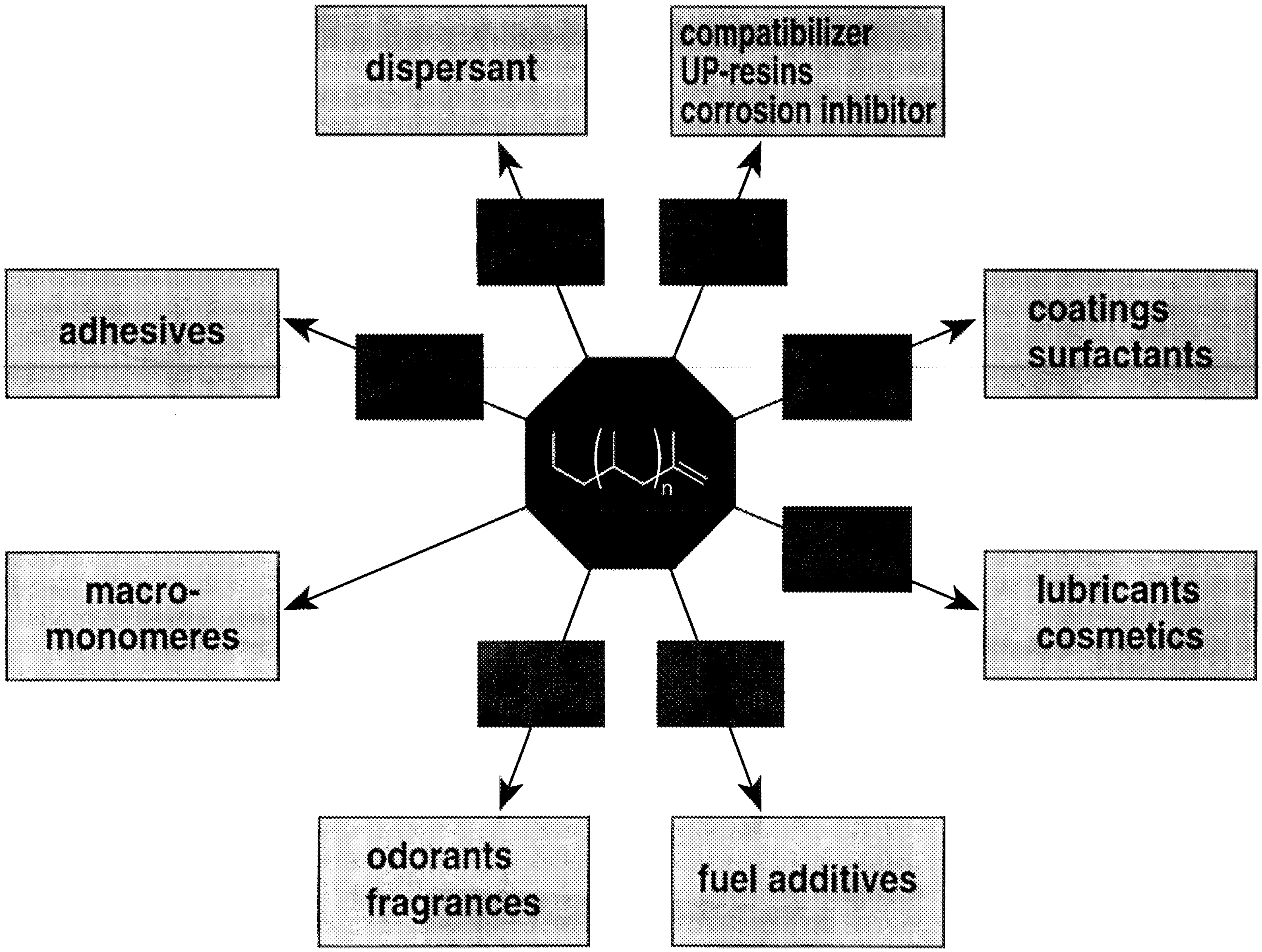


Figure 18. Comparison between conventional and metallocene polyethylene

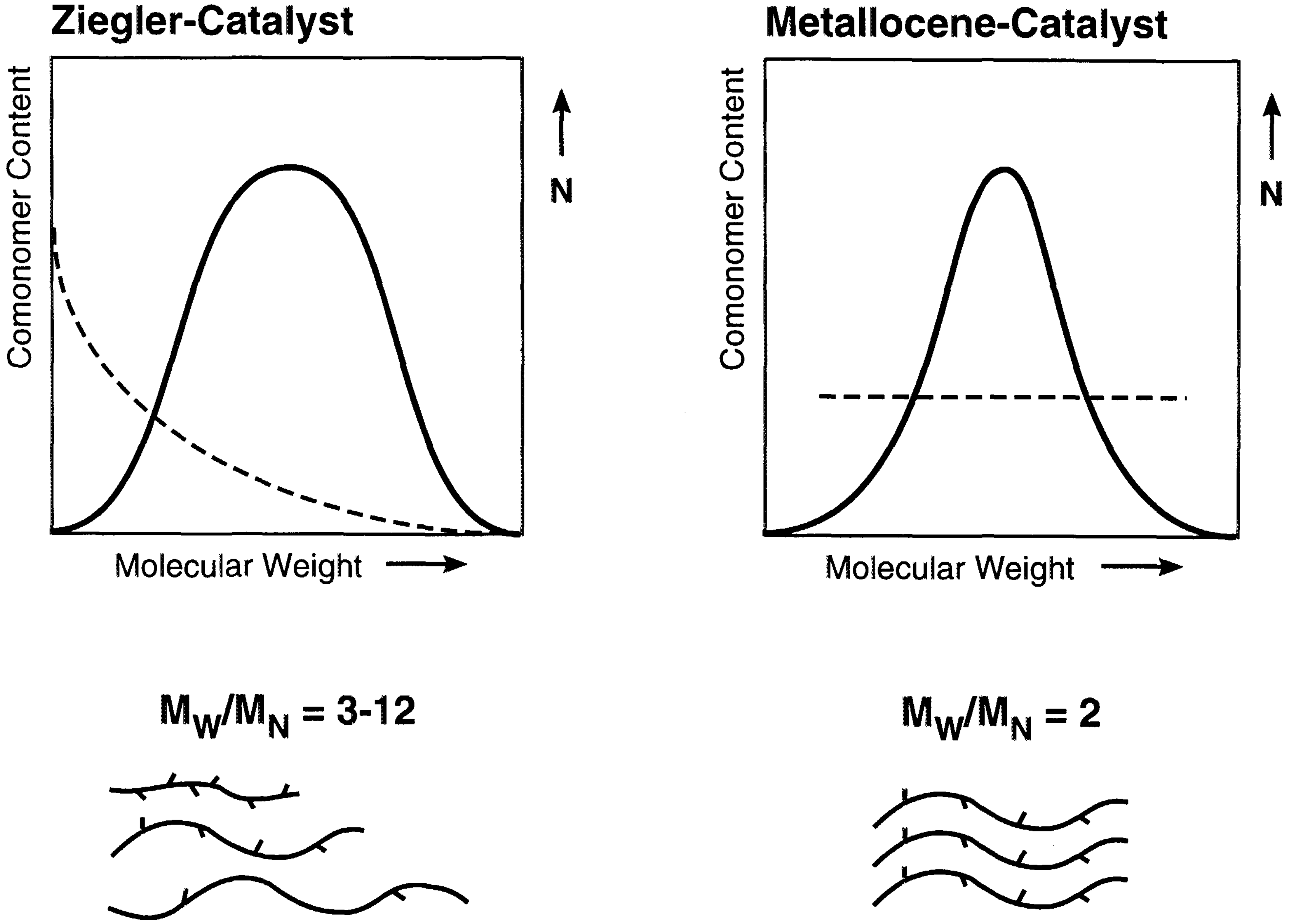


Figure 19. TREF plot of conventional and metallocene polyethylene

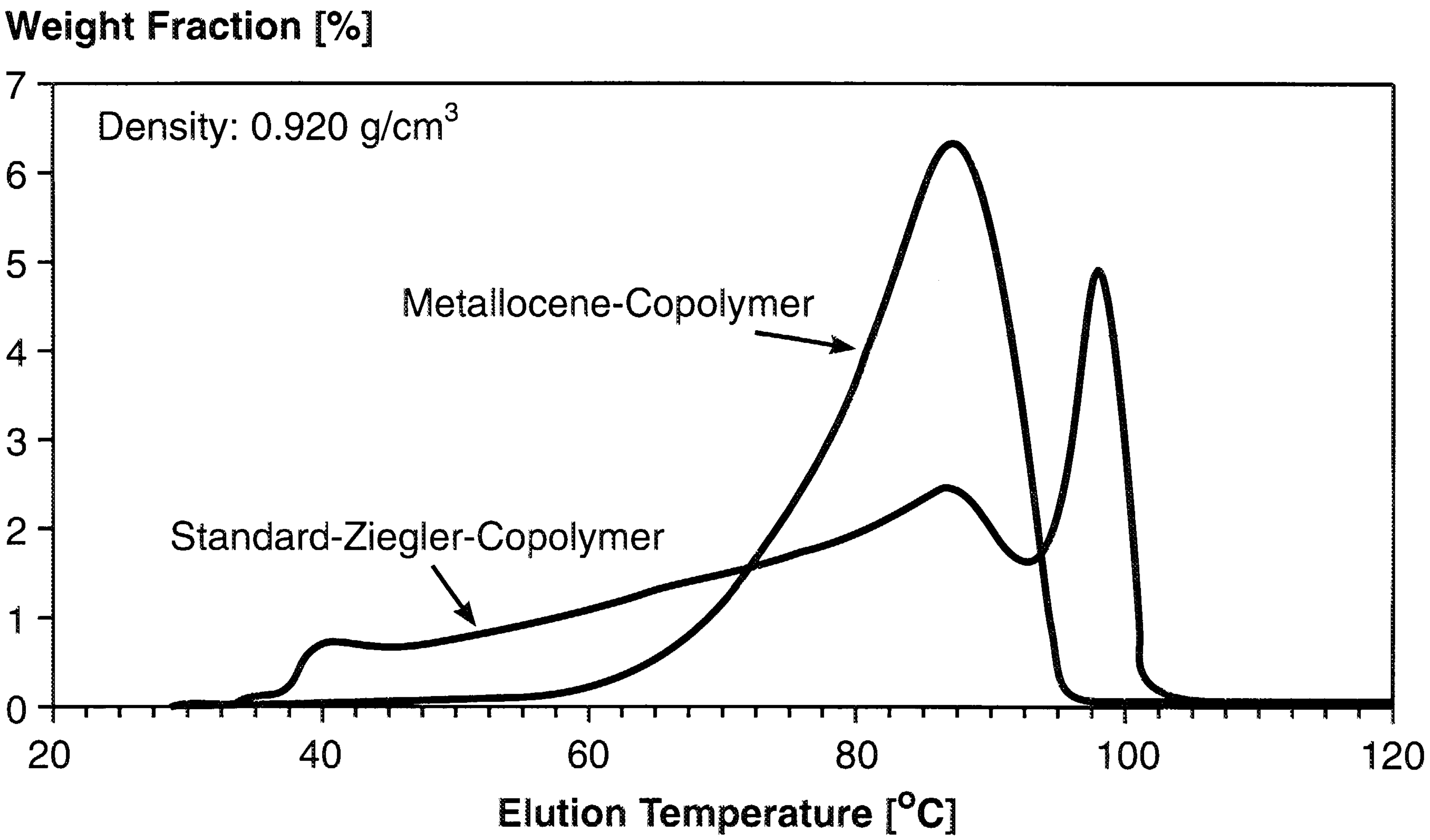
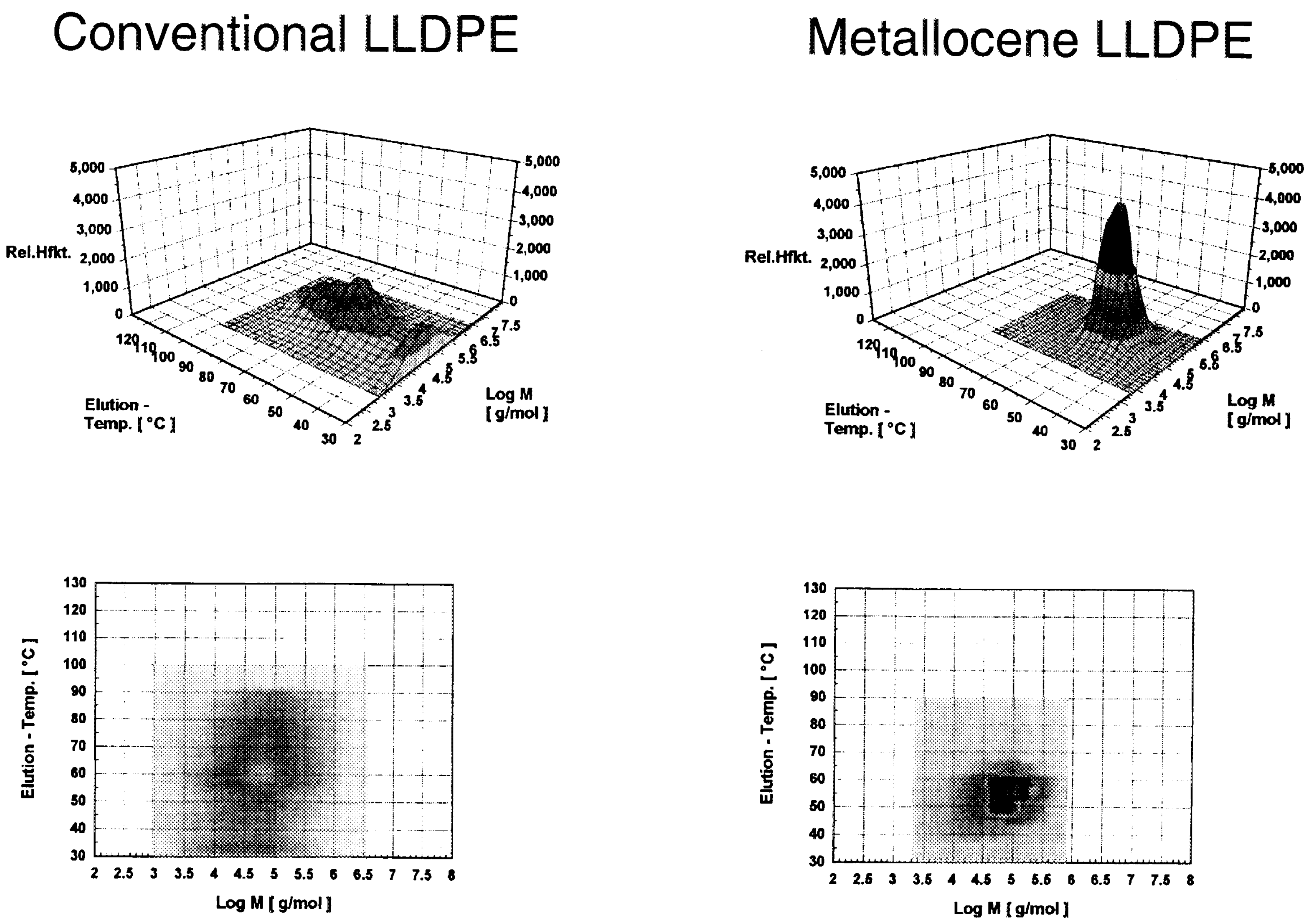


Figure 20. Cross-fractionation


Conventional LLDPE

Metallocene LLDPE

Figure 21. Bimodal metallocene resin with inverse comonomer distribution

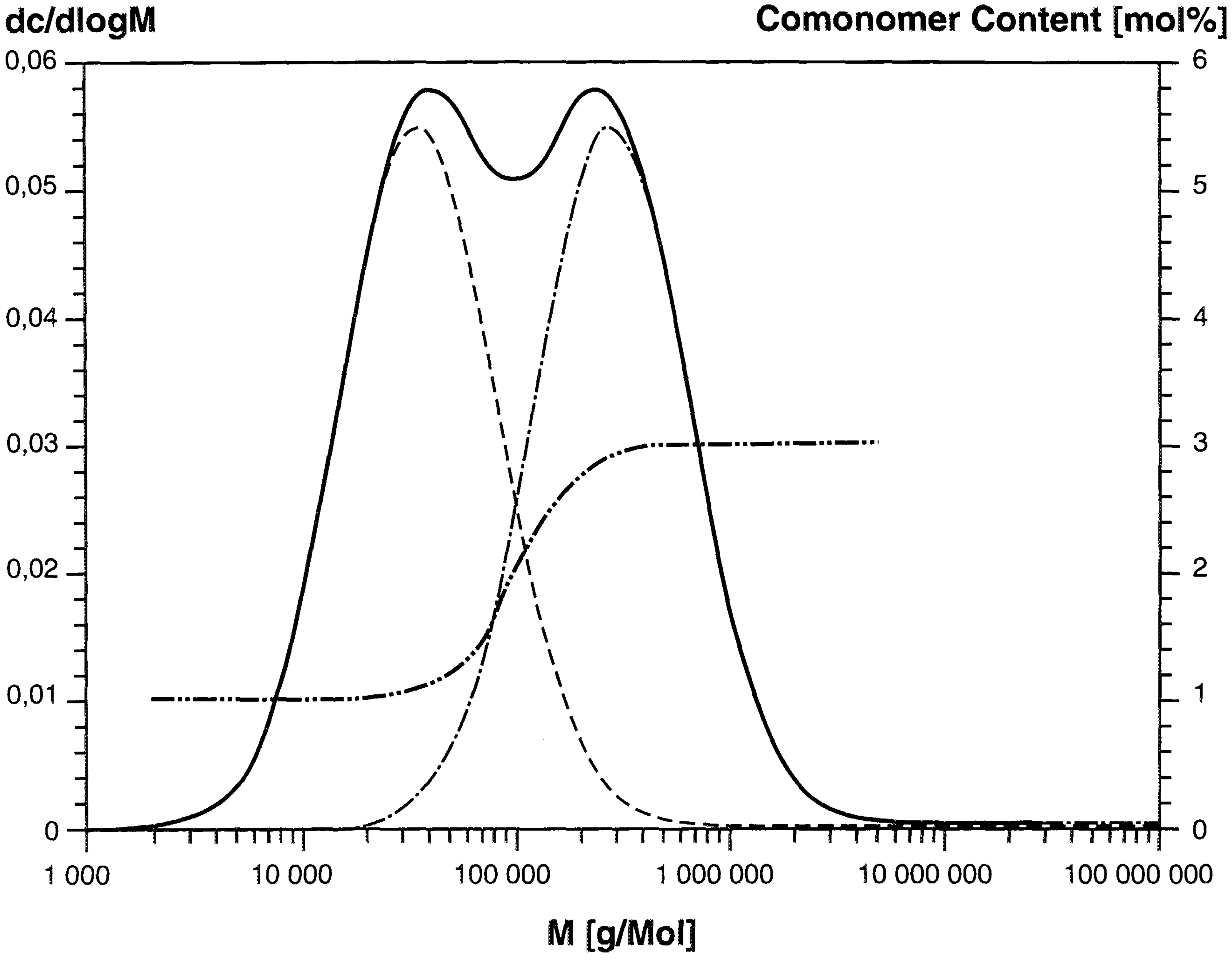


Figure 22. Metallocene crystallization behaviour

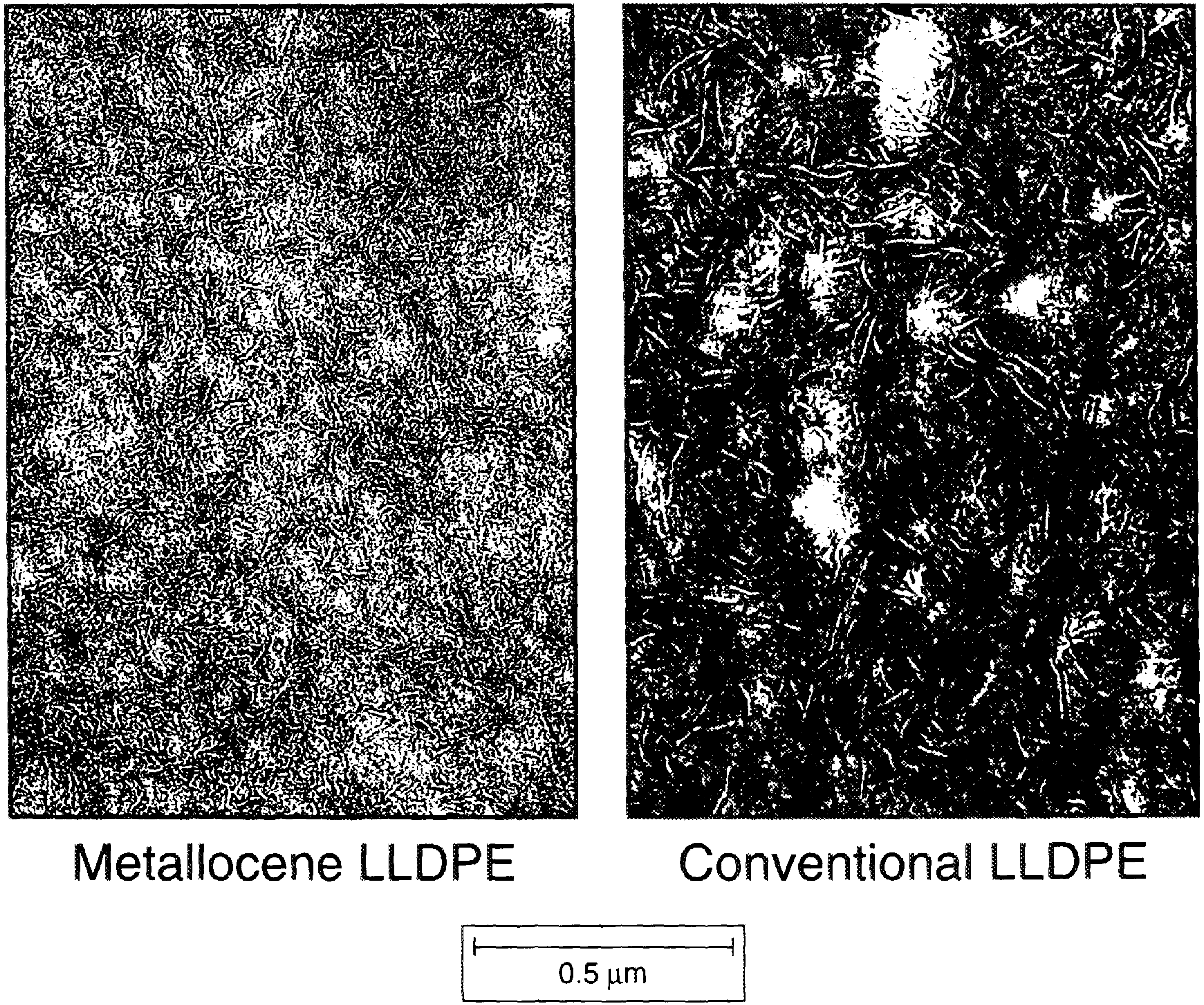
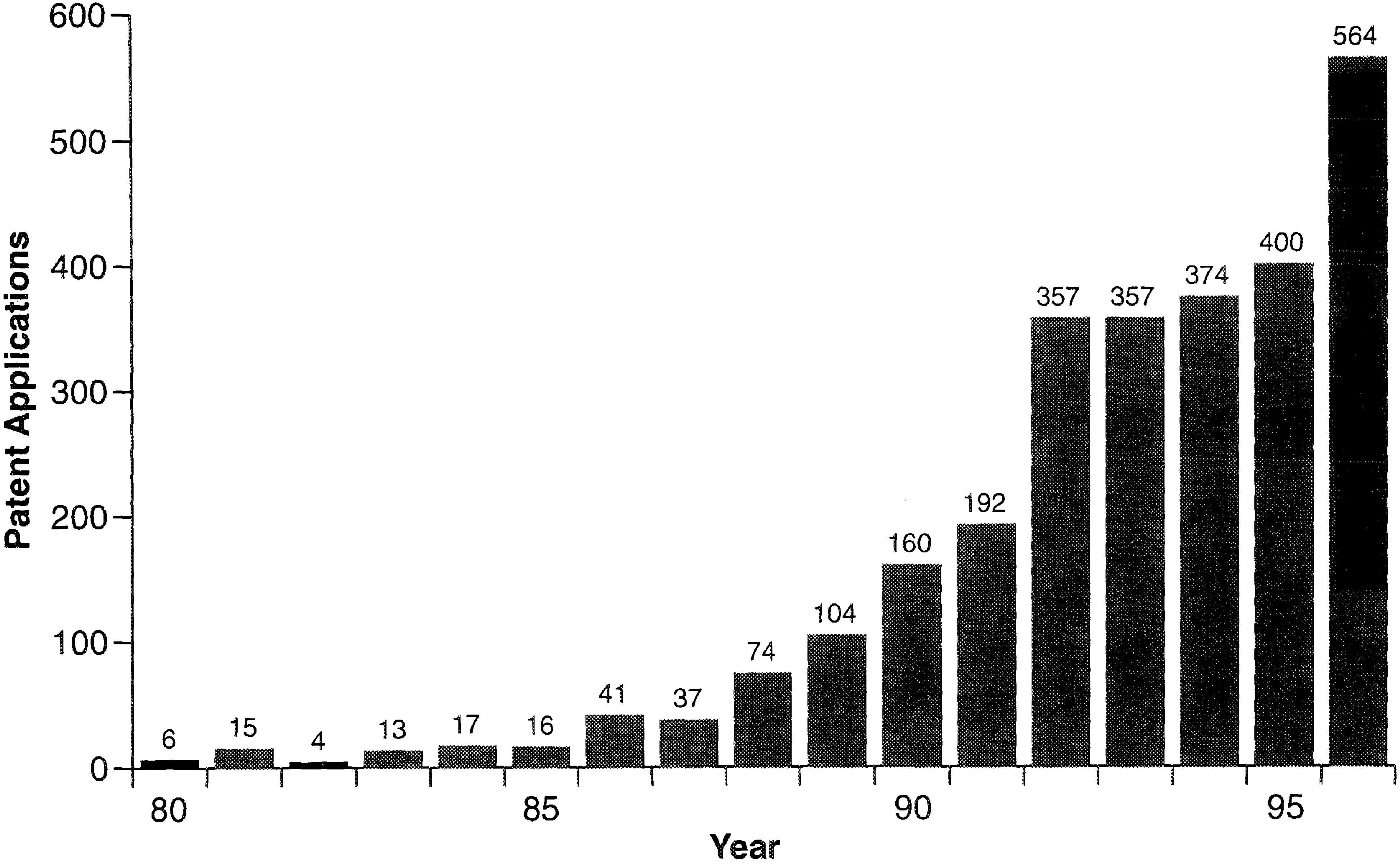


Figure 23. Film properties of polyethylenes

	Luflexen Butene 0322 H	Hexene-LLDPE	Z/N-Hexene-LLDPE
Thickness [µm]	40	40	40
Density [g/cm³]	0.903	0.919	0.919
Haze [%]	2	10	14
Dart Drop [g]	>1400	1185	100

Figure 24. Puncture resistance test of Luflexen 0322 H

Figure 25. Patent applications filed on metallocenes



B. RESEARCH TRENDS

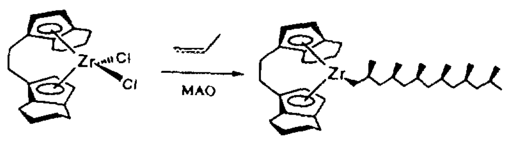
Contemporary Metallocene Technology

Author: Dr. Peter Margl

Introduction

The discovery of catalytic olefin polymerization by Karl Ziegler in 1953 and stereoselective α-olefin polymerization by Natta in 1954 are among the most important developments in polymer science. Traditional Ziegler-Natta polymerization catalysts consist of heterogeneous titanium halide and alkylaluminium. Quite recently, a new and promising generation of catalysts for ethylene and α-olefin polymerization has emerged. The new catalytic systems (equation 1) are composed of a group IV metallocene complex such as **1** and an aluminoxane cocatalyst, usually methylaluminoxane (MAO).

Equation 1



ethylene bis(tetrahydroindenyl)$ZrCl_2$

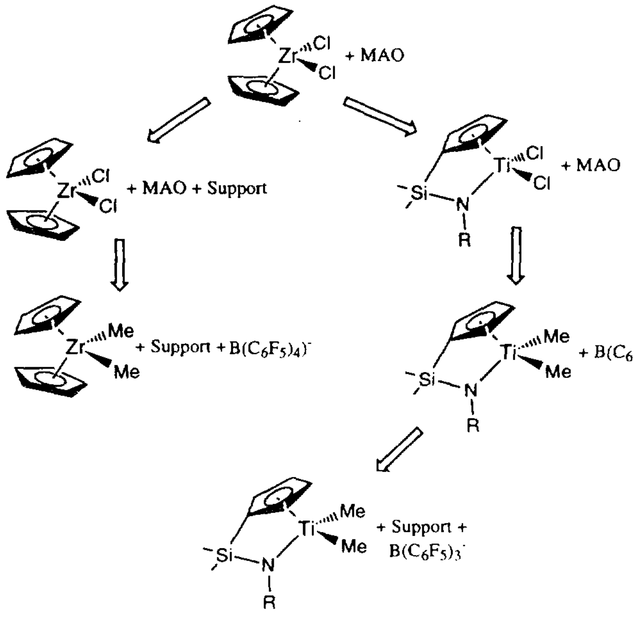
1a

This discovery has led to an impressive amount of activity in the field as the major chemical companies race towards the commercialization of metallocene-based systems. In the past few years over 250 patents have been issued for chiral zirconocene catalysts alone.[1] Metallocenes are a relatively old class of organometallic complexes, with ferrocene being the first discovered in 1951. At the time the term metallocene was used to describe a complex with a metal sandwiched between two η^5-cyclopentadienyl (Cp) ligands. Since the discovery of ferrocene, a large number of metallocenes have been prepared and the term has evolved to include a wide variety of organometallic structures, including those with substituted Cp rings, those with bent sandwich structures, and even the half-sandwich or mono-Cp complexes (see figure 1).

Metallocenes as olefin polymerization catalysts also have a long history. As early as 1957 Natta reported the polymerization of ethylene with the titanocene catalyst Cp_2TiCl_2 and the cocatalyst triethyl aluminium, a cocatalyst traditionally used in Ziegler-Natta olefin polymerization systems. The activity of the metallocene with the Ziegler-Natta cocatalyst was very low and therefore showed little commercial promise. The current interest in metallocenes originated with a discovery by Walter Kaminsky's laboratory at the University of Hamburg in the mid 1970s. While studying a homogeneous $Cp_2ZrCl_2/Al(CH_3)_3$ polymerization system, water was accidentally introduced into the reactor leading to an extremely active ethylene polymerization system. Subsequent studies revealed that the high activity was due to the formation of the cocatalyst methylauminoxane (MAO) as a result of the hydrolysis of the trimethyl aluminum, $Al(CH_3)_3$. It is because of the discovery of this new cocatalyst in Kaminsky's lab that metallocenes are also commonly called "Kaminsky" catalysts.

Olefin polymerization catalysed by metallocenes is believed to occur via the Cossee-Arlman mechanism as known from traditional Ziegler-Natta catalysis and shown in figure 2. A significant amount of experimental and

Figure 1. The evolution of metallocene olefin polymerization catalysts



theoretical evidence suggests that a cationic alkyl-metallocene complex is the active species in the polymerization. The MAO cocatalyst is believed to (i) alkylate the metallocene, forming the active complex, (ii) scavenge for impurities, (iii) stabilize the cationic centre in an ion-pair interaction, and (iv) possibly prevent bimetallic deactivation processes from occurring. The exact details of the reaction mechanism including the role of the cocatalyst are currently the topic of intense research and debate.

Since Kaminsky's discovery of the high activity Cp_2ZrCl_2/MAO ethylene polymerization system, metallocene catalysts have slowly evolved as producers push to commercialize the technology. The innovations have primarily been directed at solving the deficiencies associated with the early metallocene systems, the most serious shortcoming being that, in order to achieve the high activities, extremely high molar Al to transition metal ratios (Al:M) of between 1000-15000:1 were required. Such ratios are commercially unacceptable in terms of the cost and the amount of residues left in the polymer. (Commercial Ziegler-Natta systems typically require Al to M ratios of between 50-200:1.) A significant effort has been put into reducing the amount of MAO required and this has led to the development of many systems with non-aluminium cocatalysts, such as $[B(C_6F_5)_4]^-$ and $[CH_3(BC_6F_5)_3]^-$. Other developments include the mono-Cp constrained geometry catalysts which have been primarily developed by Dow and Exxon. These are typically titanium based and have one Cp ligand replaced by a heteroatom that is "constrained" by a bridging group. (Nitrogen is the preferred heteroatom and silicon the most preferred bridging centre as shown in figure 1.) Significant effort has also gone into heterogenizing the catalyst system by supporting the metallocene and cocatalyst onto an inorganic support such as silica. Despite all the innovations Zr still remains the most common metal centre, followed by Ti and Hf. Work has also been done with Sc, Cr, and lanthanides.

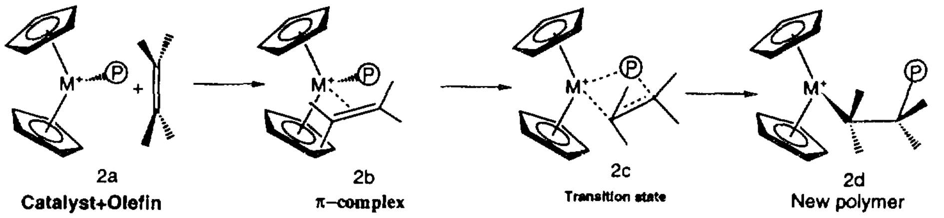
The new generation of metallocene catalysts has sparked the interest of many researchers for several reasons. First, 100 per cent of the metal appears to form a catalytically active site, with each site promoting the rapid build-up of large polymer chains. This is of commercial importance because a large amount of polymer can be produced from a small amount of catalyst. This in turn means that a smaller amount of contaminant will be found in the final product. Another reason for the interest in metallocenes is that polymers can be produced which have a high molecular weight and at the same time possess a very narrow molecular weight distribution. Metallocene based systems also give a uniform distribution of comonomer through the whole spectrum of polymer molecular weight, whereas present commercial Ziegler-Natta catalysts generally give a polymer with more of the copolymer incorporated in the low molecular weight region. Uniform comonomer incorporation yields improved polymer strength while still providing good processing properties. Metallocenes also show promise in the production of stereospecific polypropylene and α-olefin polymer. It was recently found that group IV chiral ansa-metallocenes[2] such as ethylene bis(tetrahydroindenyl)$ZrCl_2$, **1a**, could homogeneously catalyse highly isotactic polypropylene (equation 1). Metallocene based catalytic systems are potentially the most important recent development in the polymer industry. Dow and Exxon have been selling commercial metallocene based polyethylene since the early 1990s and both are in the process of ramping up production to a large scale.[3] Many other companies have also committed themselves to large-scale production of metallocene catalysed polymer in "the near future".[4] Almost all of the major chemical companies are active in the areas of metallocenes and molecular modelling—Exxon, Dow, Hoechst, Fina, Himont, Mitsubishi Petrochemicals, Chisso, Atochem, Mitsui Toatsu, Akzo, Phillips, Mitsui Petrochemicals, Idemitsu, BASF, Enichem, Bayer and others.

A new generation of research tools is also emerging that has a promising future. Computational chemistry or molecular modelling is becoming an invaluable tool in all areas of chemistry. It is already an integral part of the drug design process in the pharmaceutical industry and with the explosive growth of computer technology that is currently occurring, it will undoubtedly find utility in the commercial study of transition metal catalysis. Although molecular modelling will never completely replace experimentation, it has the potential of reducing the amount of time and the number of costly experiments done in the laboratory. It will become more and more cost-effective to simulate chemical processes on the computer as laboratory costs continue to rise and the price of computers drop.

Modelling of catalytic activity

The scheme proposed by Cossee,[5] figure 2, is the most widely accepted mechanism for Ziegler-Natta olefin polymerization. The first complex **2a** possesses a vacant

Figure 2. Cossee mechanism for Ziegler-Natta olefin polymerization



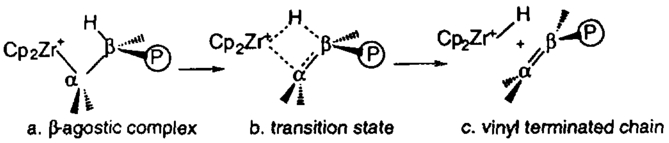
coordination site to which an olefin binds to form the π-complex **2b.** Following this, the olefin inserts into the M-C bond through a four membered cyclic transition state **2c**. The insertion forms a complex, **2d**, which is equivalent to **2a** and thus allows for the propagation of the polymerization.

The potential energy surface for the insertion process in figure 1 by DFT for a few generic systems have been published.[6] Some factors remain unknown, for instance the relative rates of insertion for ethene, propene, and butene with respect to bis-Cp and mono-Cp systems holding different substituents and various bridges. Those questions are likely to be answered in the near future, using hybrid quantum mechanical/molecular mechanics models where the close neighbourhood of the metal is modelled by high-level quantum mechanics and regions further away from the metal centre are modelled by molecular mechanics force fields.

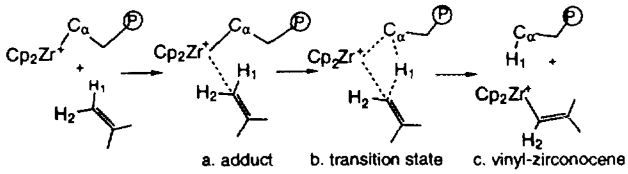
Modelling of molecular weight

On a molecular level, the chain length or molecular weight of a polymer is influenced by a number of competing processes. Throughout the polymerization, the propagation reaction must compete with a host of different processes which may terminate the growth of the polymer chain. Possible termination processes are beta-elimination, olefin C-H activation, methyl elimination and any reaction which may destroy the catalyst itself.[7] Based on this concept, trends in the molecular weight can be modelled by determining the activation energies for the chain terminating processes and comparing them to the activation energy of the chain propagation reaction. These relative energies could then be used to gauge the metallocene's propagation ability and thus reveal trends in the polymer molecular weight produced by each catalyst. The following termination steps are of interest.

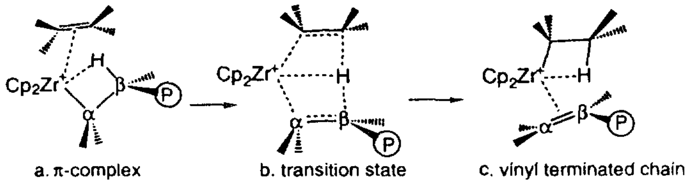
β-hydride elimination :



sigma bond metathesis :



hydride transfer :



Modelling of copolymerization and long-chain branching by metallocenes

The copolymerization of ethylene with α-olefins can lead to linear polyethylene modelling of copolymerization and long-chain branching by metallocenes with short-chain branches. Their properties and commercial value depends considerably on the comonomer content and distribution. Alternatively, long-chain polymers can be produced by the reinsertion of vinylic end groups of polymer chains eliminated by β-hydride transfer or other chain termination mechanisms.

The possibility of controlling the properties of short- and long-chain polymers by metallocene catalysts will likely be the subject of future investigation. Studies of how the comonomer content and distribution is determined by factors such as the ligand environment and nature of the metal can be carried out by combined QM/MM as well as pure MM calculations.

Modelling of solvent effects and the interaction between the active site (catalyst) and the stabilizing anion (co-catalyst)

Jordan[8] has established that the active group IV metallocene catalysts can be formulated as the cationic species $[Cp_2MR..olefin]^+$ bound to an anion A^-. According to the intermittent growth model by Reichert,[9] an equilibrium seems to exist (see Scheme I) between a dormant ion-pair, $[Cp_2MR]^+A^-$, and the active olefin complex $Cp_2MR..olefin]^+A^-$. The structure of MAO is not known exactly. However, Barron[10] and co-workers have shown that species of the form $(\mu_3\text{-}O)_6Al_6(t\text{-}but)_6Me^-$ might be active as A^-.

Scheme I

Intermittent growth model

$[Cp_2MR]^+A^-$ + olefin ⟶ $[Cp_2MR..olefin]^+A^-$ ⟶ Insertion

Dormant Species **Active Species**

It is known experimentally that substitutions of hydrogens on the Cp-rings with more bulky groups will increase the activity of metallocenes, in particular towards propene and butene, although the metal centre now is sterically more congested. We hope to demonstrate that this is associated with a weakening of the ion pair interaction in $[Cp_2MR]^+A^-$ which makes the formation of the active species $[Cp_2MR..olefin]^+A^-$ more facile. Other counter ions are used, though not in industrial applications, in particular the boron systems investigated by Marks[11] and others.

Computational molecular modelling is becoming an invaluable tool for chemists of all disciplines and is expected to change the way chemistry is done, while in the area of commercial olefin polymerization, Kaminsky catalysts or metallocenes are also expected to be revolutionary. If metallocene technology lives up to only part of the potential shown in the lab, much of the current Ziegler-Natta polymerization technologies will become obsolete.

Molecular modelling is already changing the way chemistry is done, for instance in the pharmaceutical industry, where it is an integral part of the drug design process. With the rapid advances now being made in computer technology, molecular modelling will undoubtedly find utility in the commercial study of transition metal catalysis as well as in other important areas. Despite its successes in organic chemistry, there is still some development required for its practical application to transition metal and organometallic chemistry.

For more information contact: Dr. Peter Margl, Dept. of Chemistry, University of Calgary, 2500 University Drive NW, T2N 1N4 Calgary, Alberta, Canada. Fax: +403 289 9488; email: pmargl@acs.ucalgary.ca

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Single-site, non-metallocene catalysts

When Lyondell Petrochemical Co., a large merchant producer of ethylene in Houston, TX, bought the polyethylene production side of Occidental Petroleum in May 1995, it saw 1.5 billion lb/year of plastic as a value-added downstream business to soften ethylene price swings and consume monomer. But Oxy's Alathon PE group added more value than Lyondell ever dreamed of.

The surprise was a sheaf of major single-site patents, applied for by Oxy, but awarded after the sale to Lyondell. And still more important patents are pending.

At least one of Lyondell's patent applications uses fundamentally different chemicals, including several that were never associated with catalyst activity before, to control a single active site. The Catalyst Group in Spring House, PA, in its December Metallocene Monitor newsletter, compares it in importance to DuPont Co.'s 500-page nickle-palladium catalyst patent last year, widely noted in the chemistry industry press at the time.

What Oxy's Alathon group had invented includes two entirely new classes of single-site catalyst based on six-sided rings, or "hetero-atom ligands", where metallocene catalysts use five-sided cyclopentadiene rings to control access to the active metal site. One is completely non-metallocene, based on bora-benzene rings, and used with zirconium and other metals. Bora-benzene catalyst make a series of unusual, narrow molecular weight distribution (MWD) olefinic polymers and copolymers (described in US Patent No. 5,554,775, issued 10 September 1996).

The new bora-benzene catalysts also have unusually high activities, which means they can be used in very small quantities. They appear to have better activity at higher temperatures than metallocenes and may be preferable in solution reactors with ethylene, the patent says. They appear to work in gas phase and slurry processes too.

The second group (described in US Patent No. 5,539,124 issued 23 July 1996) are azametallocene, or half-metallocene.

They use a pyrrolyl ring fused to an aromatic ring, bridged to a cyclopentadiene ring. In previous literature, pyrrolyl rings, which contain nitrogen, are considered inherently unstable and not suitable for catalysts.

The trick is fusing them to the aromatic rings, which results in very high catalyst activity, the patent says.

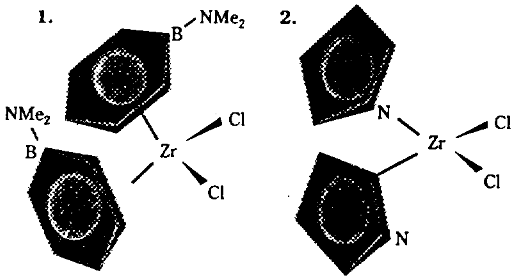
They produce colourless polymers having superior ultraviolet stability and long-term stability according to the patent.

They are also easier to make and less expensive than metallocenes, the patent adds, and can be used in slurry, solution, high-pressure or gas phase reactors. Solution, however, is the preferred method.

Lyondell is waiting on at least two more recently published world patent applications for new catalysts, including more novel six-sided ring structure. A World Patent Application (WO 96/33202 published 24 October 1996) describes a catalyst based on pyridine or quinoline, heretofore unsuspected of possessing any catalytic properties. The pyridine/quinoline patent application is the class that got high marks in the Metallocene Monitor.

Resulting polymers are described as having very high molecular weight, as seen from their low melt indexes (MI). Many are below 0.01 g/10 minutes, some are still below 0.01, even under high load test conditions. These catalysts can also be quasi-metallocene, as they describe possible bridging to a cyclopentadiene ring. (Source: *Plastics World*, April 1997)

The shapes of two new single-site catalysts just patented by Lyondell



Six-sided borabenzene catalyst **Nitrogen-containing azametallocene catalyst**

Source: U.S. patents # 5,554,775 and 5,539,124

Note the six-sided rings of the borabenzine catalyst, which distinguish it from metallocenes, and the nitrogen element on the azametallocene catalyst, previously thought to be unstable. They are part of a surprise collection of unusual catalyst work from Alathon.

C. NEW DEVELOPMENTS

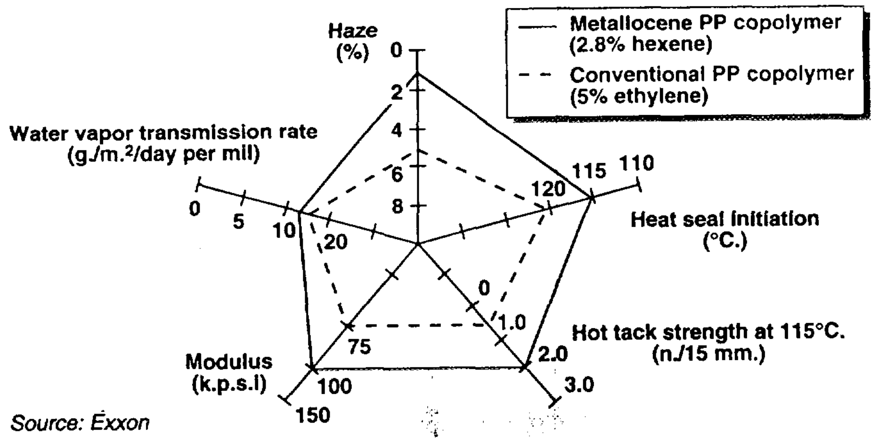
Metallocene-catalysed PP grades move closer to commercialization

Radically new versions of polypropylene (PP) with above-conventional processing and property balances have been described by two PP suppliers. In separate announcements in September 1995, Exxon Chemical Co., Houston, TX, USA, and Amoco Chemical Co., Chicago, IL, USA, detailed use of metallocene catalysts to create high-performing PP variants.

Exxon has used metallocene catalysts in a commercial PP reactor, and has synthesized hexenepropylene random copolymers. Film, moulding and fibre grades will soon be commercial.

Amoco developed a process that gives PP homopolymer properties similar to impact copolymer. Impact copolymers and PP-based elastomers are now made by extra reactor or compounding steps.

Metallocene PP copolymer stretches cast monolayer film's properties



Source: Exxon

Experts see mPP cannibalizing many PP markets and expanding the polymer's role by replacing other plastics and non-plastics.

Since the early 1990s, metallocene-based polyethylenes have been available from Exxon and Dow Chemical, Midland, MI, USA, and in Japan, from Mitsui Petrochemical, Tokyo. Now the focus is shifting to metallocene-based PP. The introduction of mPP could expand the PP market by 45 per cent over the next few years.

Exxon's products, tradename Achieve, are the first of an mPP family to be made on its bulk slurry units in Baytown, TX, USA. The catalyst was jointly developed by Exxon and Hoechst AG, Frankfurt, Germany, under a cooperative agreement that leaves each free to exploit the technology independently. Exxon officials expect the catalyst to be viable in all reactor units (including gas-phase) without modification.

The new catalysts make isotactic PP that is more versatile and precise than that made with conventional catalysts. The mPP polymers have a wider range of melt points (120° C to 164° C) and a superior balance of physical properties than existing PP. And Exxon's resins process at up to 70° C lower temperatures than conventional PP.

Moreover, higher alpha olefin comonomers now synthesize with the new catalysts, producing random copolymers with above-conventional properties.

Another benefit of mPP is that melt-flow can increase without controlled rheology, which involves the use of organic peroxides to visc-break the PP molecule, adding cost and residuals.

Finally, mPP minimizes atactic content (a fraction of 1 per cent, versus 3 to 4 per cent for PP), improving physical and organoleptic properties. (Source: *Modern Plastics International*, October 1995)

Polyolefins tailor-made with metallocene catalysts

Polyolefins with such highly-sought physical properties as adhesion, dyeability, paintability, printability, and compatibility with other polymers have been developed by researchers at Pennsylvania State University, University Park, PA. These characteristics have been produced by combining metallocene catalysts with borane polymers and "living radicals".

Metallocene catalysts are promising because they create unsaturated chain ends when polymerizing polyolefins. The unsaturated chain ends then become sites for boron additions to the polymer, creating borane-terminated polyolefin.

These borane groups are versatile intermediates that can be used as substitution sites for attachments of functional groups, and can also create living radicals for further polymerization. With metallocene catalysts, two monomers can be equally incorporated regardless of their relative size, allowing creation of uniform composition plastics. Another benefit of these catalysts is that they use monomer more efficiently, wasting less material in the polymerization process.

Using a combination of metallocene catalysts, borane polymers and living radicals, it might be possible to create future copolymer blends with predictable characteristics. Controlling the location of functional groups will control the plastics structure. In this way, plastics with specific crystalline structure or melting points could be designed for specific applications.

For more information, contact Dr. T.C. Mike Chung, Pennsylvania State University, 312 Old Main, University Park, PA 16802-1504. (Source: *Advanced Materials & Processes*, May 1996)

Advances in science trigger opportunities

Catalysis has gained a reputation among some observers as a mature science. Speakers at the 11th International Congress on Catalysis in Baltimore pointed to a series of advances, including the development of metallocenes and improvements in selective oxidation catalysts, as strong evidence of the continuing opportunities. At the same time, scientists described the growing sophistication of analytical and computational techniques, which are making the prospects of rationally designed catalysts increasingly feasible.

The focus of catalyst research has largely shifted from petroleum and petrochemical catalysts towards research on fine chemicals, pharmaceuticals and agrochemical catalysts.

Nowhere are the stakes higher than in the development of single-site metallocene catalysts. The most valuable feature of single-site catalysts is that they allow chemists to fine-tune the molecular structures of polymers, producing products ranging from high-molecular-weight elastomers to high-density polyethylenes.

Metallocenes give a tremendous degree of control over monomers. The beauty of them is that there are so many places where you can logically hang functional groups onto the polymer backbone. In addition to the polyethylenes being commercialized, metallocenes are making possible a series of novel copolymers, including an ethylene-styrene compound that Dow is testing in a pilot plant.

Still, much of the research presented at the Baltimore conference centred on traditional areas of catalysis. Finding more effective catalysts for highly selective oxidation reactions, for example, remains a key goal.

Selective oxidation enjoys a lot of attention because it is one area of catalysis that still has not achieved high levels of yields and selectivities. Chemists want to expand the use of oxidation processes, targeting goals such as making propylene oxide directly from propylene. In addition, researchers would like to use hydrogen peroxide—and even oxygen—as oxidizing agents.

Experts say EniChem's development of titanium silicates (TS-1) catalysts points to the potential of using hydrogen peroxide as the oxidizing agent in selective oxidation reactions. The TS-1 catalysts can be used to make various epoxides and have been commercialized for several processes.

The increasing use of synchrotron radiation for *in situ* characterizations is providing particular insights. After years of preparation, catalysis researchers at DuPont, Dow and Northwestern University gained access in July 1996 to Argonne National Laboratory's (Argonne, IL) newly constructed Advanced Photon Source. The facility provides X-rays that can be used to monitor catalytic reactions in real time under reaction conditions. Synchrotron experiments also continue at Brookhaven National Laboratory (Brookhaven, NY).

The synchrotron experiments are critical because they reveal in real time the changes in a catalyst during a reaction, as well as the formation of intermediate chemical species. For example, researchers working at Brookhaven are examining the oxidation states of catalysts used in butane oxidation. The objective is to understand how the oxidation states change during the reaction and to identify the state responsible for catalysing the reaction.

Scientists are also turning to molecular simulation to gain insight into rationally designing catalysts. While industrial researchers have adopted such computer modelling to help characterize catalysts and understand physical properties of the materials, a more ambitious goal is to understand the chemistry of catalysis. (Source: *Chemical Week*, 7 August 1996)

Borealis debuts PE slurry process

Borealis says it is commercializing metallocene-based polyethylene (PE) made using its slurry loop process. The company, which reports full-scale test runs with its metallocene catalyst at its Ronningen, Norway slurry loop PE plant, says it expects to make 30,000 tons per year of metallocene PE in 1997 and will market the products under the Borecene name.

To clear the way for the production, Borealis says it has formed a patent licence agreement with Exxon Chemical that allows Borealis to use its metallocene technology in slurry processes in Europe and market the metallocene PE worldwide.

The deal represents Exxon's first licensing agreement covering the use of metallocenes in slurry loop PE processes, a potentially large retrofit market for metallocene technology. Industry experts say that metallocenes could help revive slurry PE technology, significantly boosting its competitiveness with gas-phase processes in making linear low-density PE (LLDPE).

In 1996, Exxon announced plans to convert slurry capacity at its facility in Baton Rouge, LA, to metallocene production. BASF has also commercialized metallocene LLDPE using its slurry process. Philips Petroleum reports testing the use of metallocenes in its slurry loop reactors.

Exxon is forming a joint venture with Union Carbide to develop, manufacture and license metallocenes for use in PE production, but Exxon says the Borealis agreement is separate from that venture, which is scheduled to begin operating in the first quarter of 1997. (Source: *Chemical Week*, 1/8 January 1997)

"Non"-metallocene catalysts launched

Tosoh of Japan is developing non-metallocene catalysts which are claimed to produce better polymer properties than conventional metallocenes.

These new homogeneous phosphametallocene-based catalysts have a similar framework to metallocene catalysts but a unique phospholyl anion ligand.

The structure consists of a zirconium-based organometallic complex and is said to offer improved processability, high activity and broader molecular weight distribution polymers than are possible with conventional metallocenes.

Processability has been a major problem in the development of metallocenes due to the narrow molecular weight of the product, a disadvantage which the new catalyst system is claimed to overcome.

Another emerging trend is the use of multi-stage reactors by metallocene producers, to get a product that is easier to process. (Source: *European Chemical News*, 20-26 January 1997)

Metallocene alternatives

Metallocene catalysts are posing problems for plastics producers, especially because of the thicket of patents held by companies such as Dow and Exxon. Canadian polyolefin producer Nova has now developed a non-metallocene catalyst which, it claims, can surpass those made with metallocenes.

Metallocene catalysts promote the formation of polymer strands with a narrow molecular weight distribution, giving a product that is stronger and more transparent, but less processable, than those made with Ziegler-Natta catalysts. Nova claims that its catalyst produces resins that are "as good as or better than metallocene polyethylene resins in many applications". The broader molecular weight distribution makes them more processable, but the mechanical and optical properties are not sacrificed, the company claims. (Source: *Process Engineering*, February 1997)

Metallocene PEs could put a new spin on rotomoulding

High-performance polyethylene (PE) resins for rotational moulders, based on new metallocene-type catalysts, were the highlights among new product announcements at a recent meeting of the Association of Rotational Moulders, held in Vienna, Austria. New mPE families were unveiled by Borealis A/S, Lyngby, Denmark, and Dow Plastics, based in Horgen, Switzerland, and Midland, MI, USA. Earlier, Exxon Chemical, Houston, TX, USA, and Novacor, Calgary, Alberta, Canada, also floated mPEs for rotomoulding, while Mobil Chemical, Edison, NJ, USA, has a line in development.

These suppliers agree that mPE grades cycle faster than conventional rotomoulding PE grades. The mPEs have a higher flow and offer better sintering qualities, improved warpage control, and enhanced mechanical properties.

Suppliers say the best prospects for mPE materials are tough, downgaugeable markets using about 0.940 g/cm^3 density resins.

Although Novacor has mPEs for rotomoulding in development in its Sclair solution process, it sees the gas-phase Unipol PE process (licensed by Union Carbide Corp., Danbury, CT, USA) as still producing the most cost-effective LLDPEs for the US rotomoulder. (Borealis and Dow have until now concentrated on Europe.) (Source: *Modern Plastics International*, February 1997)

BASF reports MAO alternative

Scientists at BASF say they have developed a metallocene catalyst system that uses an ionic activator, avoiding the use of methyl aluminoxane (MAO). Typically, supported metallocenes require the use of MAO to achieve high activity in polymerizing olefins. However, MAO is expensive and poses potential safety problems. Details of BASF's technology were presented at the Metallocene Europe '97 Conference in Düsseldorf.

BASF says it uses cationic activators, such as boron-cocatalysts, and has developed an efficient method of depositing the cocatalysts and metallocenes together on a silica support. BASF says the catalyst system is less expensive than existing metallocene technology and that the cocatalysts can be used with various types of metallocenes. In addition, BASF says tests indicate that the catalyst system can be used to make a range of different resins.

The company reports testing the catalyst system in slurry and gas-phase polyolefin reactors and says it is scaling up the technology. Tests in a slurry-loop pilot plant showed the technology can easily be used to make the company's commercial metallocene-based polyethylene product, Luflexen, according to BASF. (Source: *Chemical Week*, 5 February 1997)

Chisso catalyst for iPP

Japanese firm Chisso Petroleum has developed a metallocene catalyst for the production of isotactic polypropylene (iPP).

Chisso now has the capability to produce polypropylene homopolymers, ethylene-propylene random copolymers and ethylene-propylene impact copolymers.

The metalllocene isotactic polypropylene resins have a narrow molecular weight distribution, with higher heat resistance and better stiffness/impact balance in injection moulding compared with conventional Ziegler-Natta resins.

In film applications, the resins extend the limits for low melting point heat sealing materials and have lower shrinkage. (Source: *European Chemical News*, 10-16 February 1997)

Paramins unveils new additives based on metallocene technology

Paramins, an Exxon Chemical Company business unit, has developed a new class of additive chemistry based on metallocene technology. Paramins is the first automotive lubricant additive manufacturer to adopt metallocene technology as the basis for a new generation of lubricant additive chemistry, according to Exxon.

The new technology is an advanced detergent inhibitor chemistry that will be marketed initially for passenger car motor oil applications. Commercialization of the product is slated for the second half of 1998.

Derived from Exxon's Exxpol metallocene technology, this detergent inhibitor chemistry represents a solid investment in new production facilities.

The new technology employs a new class of copolymers which are highly soluble and unsaturated. The new detergent inhibitor chemistry will mean better overall performance, including fuel economy and corrosion prevention, as well as greater flexibility in the selection of base stocks, according to the company.

The technology means Paramins can configure new additive packages as specifications in the motor oil industry evolve. The company says this will allow for a wider range of formulation options once new industry specifications are finalized, and that the new technology meets or exceeds current specifications. (Source: *Chemical Market Reporter*, 24 February 1997)

Dow claims resins are the Elite

Dow Plastics' enhanced polyethylenes made with its **INSITE** single-site catalysts are said to process as well as, or better than, conventional LLDPE resins on existing blown and cast film processes. The claim was made at the commercial launch of the first four grades of Dow's **Elite** PE resins.

According to Dow's commercial director for PE in Europe, competing PEs based on metallocene technology offer improved performance but often with a sacrifice in processability. He said the **Elite** resins offer outstanding property combinations while maintaining good processability. This processability advantage is another distinct point of differentiation between **Elite**-enhanced polyethylene resins and current competing metallocene LLDPEs.

A feature of the **INSITE** catalyst is its "constrained geometry" which forces greater exposure of the active metal site. It allows the incorporation of long chain branching into the polymer structure to give easier processing. Dow also pointed out that **INSITE** is chemically different from other metallocene catalysts.

The technology gives precise control of the polymer structure and resulting properties. It gives property combinations not possible with conventional PEs, said Dow, giving examples of high stiffness and impact strength, or high stretch and high puncture resistance.

The first four **Elite** resins will have thick- and thin-gauge consumer and industrial blown film applications, cast stretch film outlets and high performance film uses. They will meet US FDA compliance regulations for direct and indirect food contact applications. Plans are under way to expand **Elite** resins into non-packaging applications such as injection and rotational moulded goods and health and personal care products, as well as building and construction products. (Source: *European Chemical News*, 10-16 March 1997)

Montell applies metallocenes to copolymers

Montell is applying metallocene catalysis to the production of polyolefin elastomers. In addition, the group plans to develop metallocene technology for the *Spherilene* polyethylene (PE) and *Spheripol* polypropylene (PP) processes.

The process, described as mixed catalysis reactor granule technology (MCRGT), is being developed on a pilot plant producing 100 kg/h of ethylene/propylene copolymers at the Natta Research Centre in Ferrara, Italy.

The proprietary co-catalyst being developed by Montell is said to be based on simple, low-cost components—among these are aluminium alkyls. The catalyst system is also claimed to have a very high catalytic activity.

The development of the metallocene process will enable the fine-tuning of the intramolecular properties of elastomers.

The narrow molecular mass distribution and controlled chemical composition, along with the absence of side reactions avoids the formation of gels or indispersable particles.

The new copolymer microstructures made available through the application of metallocene technology will enable new structures and properties to be realized.

This creates the opportunity of producing new EPDM grades and expanding traditional areas of applications.

Montell describes the process as a "drop-in" replacement for existing EPDM grades. It is currently being pilot tested in gas-phase reactors but is also being trialled in slurry and solution reactors. (Source: *European Chemical News*, 14-20 April 1997)

Innovation in action—Developing high performance polyethylene technology

The **Innovene** process is being continuously improved by a research and technology team working at the leading edge of process and catalyst innovation. The aim is to make resins which are cheaper to produce; convert to stronger end products; are easier to process; and meet regional and worldwide market requirements.

A polyethylene grade that processes easily into a film product having very high strength is a difficult combination to achieve. With conventional Ziegler and metallocene products there is a trade-off between strength and processability. This is why the recently announced joint technical cooperation between BP Chemicals and the Dow Chemical Company is so significant. The **Innovene** process using **INSITE**™* catalyst from Dow is unique in its ability to achieve the required combination of strength and processability in its end-products.

Long chain branching

The reason for this break with convention is Dow's patented constrained geometry catalyst which polymerizes uniformly and selectively introduces long chain branching into a very narrow molecular weight distribution polymer chain. This is the only technology to successfully produce polymers with very narrow molecular weight distribution (MWD) and good processability. The products are stronger, but more processable, than conventional Ziegler and high-pressure LDPE technology-based products. Very importantly, there is no need for expensive processing aids or to blend, and no need to change the extruder die when switching from LDPE.

The demonstration of no output penalty using existing extrusion equipment is the key to wide acceptance in high volume markets. **Innovene** with **INSITE** is clearly differentiated in this respect and has already demonstrated an increase in output compared to LLDPE in tests at commercial scale. This benefit goes beyond "easy processing" LLDPE and could transform the polyolefins industry by expanding the current limits on polymer uniformity, performance, processability and versatility.

Conventional linear low density polyethylene is produced by Ziegler-Natta catalyst with multiple active sites. Multiple active sites create polymers with varying molecular structures, resulting in variable distribution of the comonomer between polymer chains.

INSITE catalyst, in comparison, has only one active site. A single site tends to polymerize in a more uniform fashion, so that every molecule is similar—polymer chains are a more consistent length, and have more consistent incorporation of comonomer into the polymer—which results in a narrow molecular weight and comonomer distribution. This uniformity leads to exceptional, very predictable physical and mechanical properties. Both narrow MW and narrow comonomer distributions maximize critical performance properties such as toughness, sealability, clarity, and other properties important to your product application. This is a distinguishing feature of **INSITE** constrained geometry catalyst technology.

Innovene with **INSITE** is aiming to open doors for users to many applications and improved cost-performance options, for example, the opportunity of high-performance and cost-efficient products for applications ranging from packaging film, extrusion coating, wire and cable, to other consumer and industrial goods.

Complementary process technology

The efficient removal of vast quantities of heat generated by ethylene polymerization in a world-scale gas-phase reactor presents a significant technical challenge, especially with the latest generation of catalysts. Modification of the reaction loop by addition of a liquid separation and proprietary injection system (High Productivity) was a breakthrough that met this challenge and has enabled single reactors to be designed capable of making over 300 Ktpa of a full range of products. The potential of the technology has been rapidly demonstrated on two world scale **Innovene** units in Europe with immediate increase in production to new design capacities. (Source: *Innovene and INSITE* technology, January 1997)

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* Trademark of the Dow Chemical Company.

D. GLOBAL PRODUCTION CAPACITY/ POTENTIAL MARKETS

Metallocene polymers set to realize potential

Global production of metallocene-based polymers could reach 10 million tons/year by the year 2000, representing 12 to 13 per cent of world polyolefins consumption of around 80 million tons/year.

This prediction was based on a metallocene-capable capacity of almost 20 million tons/year by the year 2000, defined as commercial production capacity that has been adapted and shown to be capable of using metallocene resins on a commercial basis.

Production of metallocene-based polymers will lag a year or two behind capacity as plants are gradually switched from 100 per cent Ziegler-based to 100 per cent metallocene-based production as markets develop. But this level of penetration was not unreasonable when compared to 28 per cent penetration achieved by LLDPE in the USA in 10 years.

Global production of metallocene-based polymers was 150,000-200,000 tons during 1995. However, several commercial polyolefins facilities have since been adapted, giving potential production of over 1 million tons/year.

Metallocene polyolefins seen so far are only the tip of the iceberg, and by no means representative of the full potential of these technologies. Second-generation products show significant improvements, not only eliminating some drawbacks, but extending physical properties and property combinations.

For example, first-generation metallocene PEs opened up new potential for new resins with very low heat-seal initiation temperatures combined with excellent hot tack strength and seal strength, increasing the speed of packaging lines by a factor of three. A second-generation product, on the brink of commercialization, combines the very low heat-seal initiation temperature with much higher resin crystallinity and density. Such a resin could significantly reduce cycle times in large injection mouldings, opening up new frontiers in these markets.

Another area under development to produce second-generation performance combinations is that of alloys of two or more metallocene resins. (Source: *European Chemical News*, 11-17 March 1996)

Reacting to metallocenes

As the dust settles following the announcements of separate polyethylene (PE) technology alliances between Dow Chemical and BP Chemicals and Exxon Chemical and Union Carbide, metallocene catalysts are emerging as a major factor affecting the polyolefins business. But the announcements have also heated up the debate in the industry over how quickly and extensively metallocenes will affect polymer markets.

Metallocene advocates argue that the technology could radically redefine polymer markets, driving some existing products—and even some resin producers—out of business. Skeptics caution, however, that while the catalysts are an intriguing development, commercialization of metallocene-based products is likely to be slow and could be largely limited to speciality applications.

Both sides agree that the stakes are high. Leading metallocene players, including Dow, Exxon and Hoechst, have spent several billion dollars to develop the technology and are racing to commercialize metallocene-based products in a range of polymer markets (see following table). The most immediate impact is expected in PE. Chem Systems (London) predicts that metallocene PE could grow to a 6.3 million tons/year market by 2005, representing about 11 per cent of the combined linear low-density PE (LLDPE) and low-density PE (LDPE) markets. Others say metallocene PE could significantly expand the overall PE business by substituting for nonpolyolefins.

The early promise of metallocenes and the pressure to recover development costs have already driven a series of technology and business alliances. Most notably, Dow has leveraged its metallocene know-how to form a business partnership with DuPont in elastomers, including ethylene propylene diene monomer (EPDM) rubber, and a technology pact with Montell in polypropylene (PP). At the same time, Exxon has formed a manufacturing pact with DSM using Exxon's metallocenes and has signed an agreement with Hoechst covering metallocene PP technology.

Observers say the ongoing commercialization of metallocenes could drive additional restructuring, as technology "haves" emerge and technology "have nots" scramble to catch up. Metallocenes—and the recent development of other advanced polyolefin catalysts—could lead to further PE industry consolidation. PE and other polymers made with metallocenes and other advanced catalysts will compete with a range of polymers, including LDPE, ethylene vinyl acetate (EVA), ionomers, thermoplastic elastomers, and polyvinyl chloride (PVC).

The most dramatic changes could come in commodity PE, particularly LLDPE. The LLDPE market will be affected very rapidly. In a year there will be significant market activity for metallocene LLDPE.

Some polyolefins producers question such scenarios, however. The degree that it will substitute and replace existing products is probably overstated. In 5 to 10 years you will probably find metallocene PE, EVA and ionomers co-existing peacefully.

While speciality metallocene PE, such as elastomers and plastomers, have become a force to be reckoned with, questions remain about commodity-grade metallocene PE made using gas-phase processes. There are still some technical issues that need to be resolved for metallocenes to really come on in a huge way and replace existing products. Regardless of whether or not metallocenes sound the death knell for some polymers, the technology is certain to affect many polymer markets. Chemical Market Resources (CMR, Houston, TX) estimates North American metallocene-based PE demand will grow 25 per cent to 30 per cent/year, to 325 million lb/year in the year 2000. While much of the growth will come at the expense of existing polyolefins, the new materials will also compete in nonpolyolefins markets. CMR estimates use of metallocene PE and new generation PP in traditional North American markets for flexible PVC will reach 240 million lb/year by 2005; growth in ethylene propylene rubber applications will grow to 54 million lb/yearand in thermoplastic elastomer markets to 45 million lb/year.

METALLOCENES HEAD TO MARKET

METALLOCENE PRODUCTS	LEADING PRODUCERS	COMMERCIAL STATUS	COMPETITIVE MATERIALS
Linear low-density polyethylene (LLDPE)	Exxon Chemical, Dow Chemical, Mitsui Sekka, Mitsubishi Kagaku, Mobil Chemical	1993[a]	Conventional LLDPE, low-density PE, ethylene vinyl acetate (EVA)
PE-based plastomers	Dow, Exxon	1991	EVA, ionomers, LLDPE
Polypropylene	Exxon, Hoechst, Fina, Dow, BASF	Commercial-scale trial runs[b]	Conventional PP, engineering plastics
Polystyrene	Dow, Idemitsu	Market-development unit due on-line in 1997[c]	Polyester, nylon, liquid crystal polymers
Ethylene propylene diene monomer (EPDM)	DuPont Dow Elastomers, Exxon	Commercial-scale unit due on-line by March 1997[d]	Conventional EPDM
PE-based elastomers	DuPont Dow	1994	EVA, flexible polyvinyl chloride, EPDM, EP rubber
Cycloolefin polymers	Hoechst, Mitsui Sekka	1997[e]	Polycarbonate, glass

(Source: *Chemical Week*, 25 September 1996)

[a] Exxon has 550 million lb/year of capacity in Mont Belvieu, TX; Dow expects to start up 500 million lb/year of capacity in Plaquemine, LA by the end of the year.

[b] Exxon has launched nonwoven spunbound products.

[c] Dow-Idemitsu unit in Chiba, Japan.

[d] DuPont Dow's 90,000 tons/year plant in Seadrift, TX.

[e] *Initial quantities supplied by Hoechst-Mitsui; 3,000 tons/year pilot plant in Iwakuni, Japan.*

However, metallocene-based products will undergo their most critical early test in commodity PE markets. The Dow-BP and Exxon-Carbide licensing pacts mean gas-phase metallocene PE technology could be widely available to the industry. At the same time, Exxon has started up 550 million lb/year of gas-phase metallocene LLDPE capacity at Mont Belvieu, TX and expects to have an additional 550 million lb/year of metallocene LLDPE capacity on-line at Notre-Dame-de-Gravenchon, France by 1997. Meanwhile, Dow plans to start up 440 million lb/year of metallocene LLDPE capacity by the end of the year at its site at Plaquemine, LA, using solution-phase technology.

While conventional LLDPE is an initial target, metallocene producers also expect to compete with LDPE. Much of that market has eluded conventional LLDPE because the material can be more difficult to process than LDPE.

Other polyolefins markets could also be vulnerable to metallocenes. While development of metallocene PP has lagged metallocene PE, observers says PP markets could, long-term, be equally affected by the new technology. Hoechst and Exxon have separately conducted commercial-scale production runs, making isotactic PP at Knapsack, Germany and Baytown, TX; Fina has made commercial-scale quantities of syndiotactic PP at its facility at La Porte, TX. Meanwhile, Exxon has launched an initial line of homopolymer products for nonwoven spunbound applications—a 50 million to 80 million lb/year market in the USA.

The big potential for metallocene PP, however, is expected to come through the development of random and impact copolymers. The catalysts allow alpha-olefins comonomers to be randomly incorporated into the PP backbone. The result could be tailored PP capable of competing with certain engineering plastics.

Producers are also looking to extend metallocenes beyond polyolefin applications. Perhaps most ambitious, DuPont Dow Elastomers is looking to use metallocenes to revitalize the elastomers market.

A different landscape

Metallocene EPDM "is essentially a better EPDM" with lower capital and operating costs. While the initial metallocene EPDM is designed to look a lot like conventional EPDM, long-term objectives include the development of metallocene products with a range of elastomeric properties.

Others are using metallocenes to develop commercial polymers with novel structures to compete with high-performance materials. Dow, for one, is working with Idemitsu to commercialize syndiotatic polystyrene (PS) made using metallocenes.

Metallocene PS is meant to compete with materials such as liquid crystal polymers and polyester and nylon-based engineering plastics. It is a semicrystalline polymer that is radically different from conventional amorphous PS.

Meanwhile, Hoechst, working with Mitsui Sekka, expects to commercialize a metallocene-based cycloolefin product by 1997. The polymer has various applications, competing with polycarbonate in compact discs and with glass in health-care applications. The company estimates the potential market for the material at $200 million/year.

Despite the promise of metallocenes in various polymer markets, some polyolefins producers say they are content to keep a watchful eye on the development work. (Source: *Chemical Week*, 25 September 1996)

Japanese PE ventures boost development

Japanese firms are continuing to develop metallocene catalyst technology aggressively, with Asahi Chemical and Mitsubishi Chemical both announcing new polyethylene ventures.

Asahi Chemical is to convert a plant in Mizushima to use a metallocene catalyst to produce 40,000 tons/year of high-density polyethylene, in a process jointly developed with Dow Chemical.

Mitusbishi Chemical is planning to produce metallocene-based polyethylene at Kashima and Mizushima. It will make 100,000 tons/year of linear low-density polyethylene using Union Carbide's *Unipol* gas-phase process at Kashima.

A further 50,000 tons/year of very low-density polyethylene (plastomer) will be produced at Mizushima. Start-up for the process is scheduled for the beginning of 1998. (Source: *European Chemical News*, 24 February-2 March 1997)

BP Chemicals set to license Innovene™*

BP Chemicals has signed its first agreement in South America to license its *Innovene* gas-phase PE technology.

Petroquimica Triunfo of Brazil has signed a letter of intent to purchase a licence to manufacture 130,000 tons/year HDPE and LLDPE. The plant will be located at Triunfo's site near Porto Alegre, where the firm produces LDPE, and is set to come on stream in 1999.

The letter of intent is for an *Innovene* high productivity licence which would include high-strength hexene copolymer and an option to license technologies, including metallocene catalysts. (Source: *European Chemical News*, 3-9 March 1997)

European expansion is Insite for Dow Plastics

Dow Plastics plans to install capacity for enhanced polyethylenes based on its INSITE single-site catalyst in Europe and Argentina. The capacity will raise its total production capability to over 1.2 tons/year by the year 2000.

In Europe, Dow is planning 210,000 tons/year production capability by the first quarter of 1998 at a site yet to be determined. BSL's site in Germany was a possible contender for either a new or retrofit plant.

A 210,000 ton/year LLDPE *Dowlex* plant is already under construction at Schkopau and is due on stream in the first quarter of 1998. However, a feature of Dow's solution technology is its easy conversion to single site catalysts.

Dow also produces enhanced polyethylenes on a converted solution plant at Tarragona, Spain, although this unit is dedicated mainly to elastomer and plastomer production.

Plans in Argentina call for a plant of projected 250,000 tons/year enhanced polyethylene capacity at Bahia Blanca with an on-stream date of 2000-2001.

The project ties in with Dow's plans to expand ethylene capacity at the site from 245,000 tons/year up to 700,000 tons/year and partake in the Mega ethane gas project.

A 300,000 tons/year polyethelene plant will be built in a joint venture with Siam Cement at Mab Ta Phut, Thailand, due on-stream in the first quarter of 1999. Dow's polyethylene capacity at Fort Saskatchewan, Alberta, will be increased by 250,000 tons/year at the end of 1998.

Initial commercial quantities of the *Elite* resins are available from Dow's Plaquemine, LA, facility which now has a 200,000 tons/year capacity. Market development quantities are also produced at Freeport, TX. (Source: *European Chemical News*, 3-9 March 1997)

China to play major role in Asia polyolefin supply

China's role as a global polyeolefins importer will increase as capacity expansions in Asia come on line, according to a presentation given at the recent Asian Olefins & Polyolefins Conference in Singapore.

Chem Systems projects that by the year 2000, Asia (excluding Japan) will be a net importer of 421,000 tons of LLDPE, 545,000 tons of LDPE, and 863,645 tons of HDPE. Most resin exports would go to China. Meanwhile, capacity additions in Asia (excluding China) in 1996-1999 will add 3 million tons of capacity, equivalent to 33 per cent of the total anticipated global PE expansions.

Indonesia will soon become a net exporter of LLDPE. Additions to Korean capacity will add to that country's already aggressive export position. Malaysia, too, will join the ranks of export-oriented suppliers, and Thailand will move into a net export position for polyolefins in 1997-1998. (Source: *Modern Plastics International*, March 1997)

Japanese makers catch up in metallocene PE

US companies have dominated metallocene news lately: Exxon, Dow and Philips have announced plans to commercially produce commodity-grade metallocene linear low-density polyethylene (LLDPE). Several Japanese players have also advanced in metallocene research, however, and are gearing up for commercial production of commodity and speciality PE grades.

Tosoh will enter the business with its own metallocene catalyst, aimed at use in gas-phase processes. Tosoh will convert a 30,000 tons/year LDPE plant at Yokkaichi to produce speciality metallocene PE grades. The unit, slated to start up in September, will make Tosoh only the third Japanese producer, after Japan Polyolefin (JPO) and Mitsubishi Kagaku , to commercialize metallocene PE with its own know-how.

JPO, a joint venture of Showa Denko and Nippon Petrochemical, is commercializing its gas-phase metallocene LLDPE technology at a 3,000 tons/year pilot plant at Kawasaki, using technology developed by Nippon. Citing a good reaction from customers, JPO will increase production to 50,000 tons/year later this year by converting an LLDPE unit at the site.

Mitsui Sekka is furthest ahead in metallocene PE in Japan, mainly through joint R&D efforts with Exxon. The company already has a 50,000 ton/year metallocene-based LLDPE plant at Chiba developed through a linkup with Ube Industries. Mitusi and Sumitomo Chemical recently formed a joint venture—Nippon Evolue—that is building a 200,000 ton/year gas-phase metallocene LLDPE plant at Mistui's site at Chiba for start-up in April 1998. (Source: *Chemical Week*, 19 March 1997)

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* Innovene is a registered trade mark of the British Petroleum Company.

High-performance products in the Asian polyethylene market. A presentation at the Asian Olefins and Polyolefins Conference.

21 January 1997, Singapore. John. R. F. Steedman and Martin R. Howard, BP Chemicals Licensing Department, and Ed Gambrell, the Dow Chemical Company

Introduction

Today in Asia, tariff barriers are shielding polymer manufacturers from the real pressures of intra-regional competition and pricing. As the objective of free trade for the region is achieved and exports increase, there will be a shift in the need for product performance, differentiation and economics.

This provides a challenge to all involved in the development of technology and the market arena into which new high- performance products have the opportunity to enter and be commercially successful.

It also puts the alliances formed in 1996 between BP and Dow, and Union Carbide and Exxon into context. Both these partnerships now have the resources to accelerate technology development in advanced catalysts and metallocenes in particular, to the point that related products can break out from the small and specialized slice of the market they occupy today.

Asia is a highly attractive region in the world to suppliers of polymer technology. Rapid growth and intense competition have combined to create both an opportunity and a challenge for licensors, and in some cases has encouraged their further involvement as shareholders and marketers.

Since worldwide licensing of BP Chemicals gas-phase polyethylene process (**Innovene®**) started in 1985, the technology has evolved continuously to win licences in tough competitive environments such as North America. For example, stronger C6 LLDPE for packaging film, and easier to process broad molecular weight blow moulding resins were major advances in product performance that have become part of the standard Innovene range. Now in a joint effort with Dow, INSITE* technology will be combined with Innovene technology to produce high performance products which will provide our licensees with a competitive advantage. The same flexibility and responsiveness will be needed to meet the fast-changing technical and trading requirements of the Asian market-place. Four key success factors to allow high performance metallocene products to penetrate the volume markets are identified and addressed in this paper.

Metallocene products

Our customers tell us they want a polyethylene grade that processes easily into a film product having very high strength. This is a particularly difficult combination to achieve with conventional Ziegler and metallocene products since there is a tradeoff between strength and processability, but it presents the first key success factor.

When LLDPE was first introduced into Asia, many converters with small, low-powered extruders found the material difficult to process. A compromise had to be made by using lean blends of LL/LDPE (30:70). Now that there is acceptance of LLDPE and more availability of suitable processing equipment, rapid growth of LLDPE at the expense of LDPE is forecast for Asia. Eventually LLDPE consumption will overtake that of LDPE, similar to North America. We must learn the lesson and ensure that the introduction of new product technology meets customer requirements without the need for a further change in equipment specification.

BP Chemicals and Dow formed a partnership of choice since the Innovene process using INSITE catalyst is unique in its ability to achieve the required combination of high strength and processability in its end-products.

The reason for this is Dow's patented constrained geometry catalyst which polymerizes uniformly and selectively introduces long chain branching into a very narrow molecular weight distribution polymer chain. The result is a product that is stronger, but more processable, than LLDPE. This puts these products at a significant advantage over conventional Ziegler and high-pressure LDPE technology-based products. Very importantly, there is no need for expensive processing aids and no need to change the extruder die centre when switching from LDPE. This combination of properties goes beyond an "easy processing" LLDPE and will have a major impact in the marketplace.

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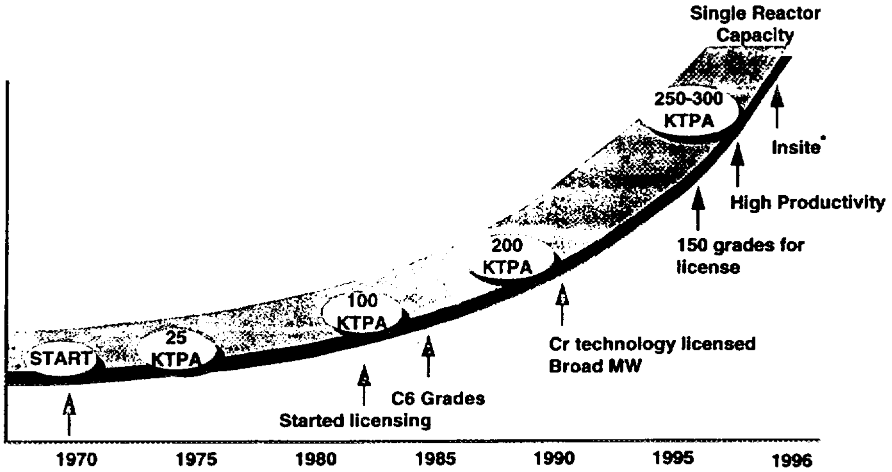
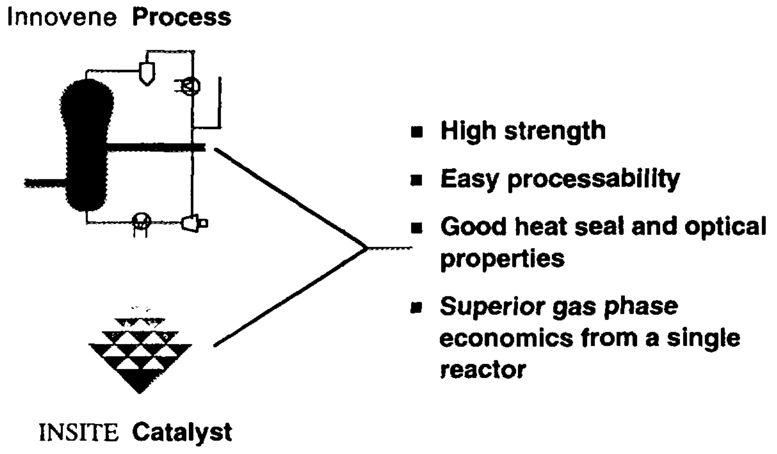
* INSITE and Dow are trademarks of The Dow Chemical Company.

Innovene process—evolution

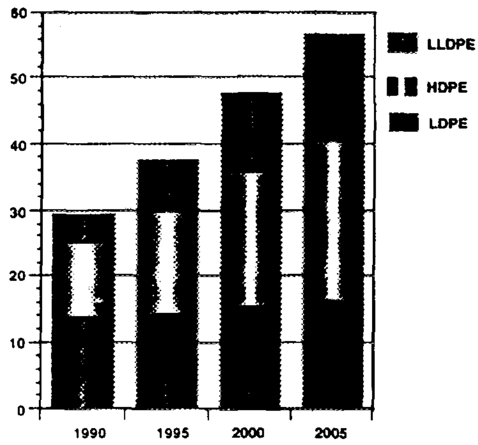


Product advantages



- High strength
- Easy processability
- Good heat seal and optical properties
- Superior gas phase economics from a single reactor

World polyethylene market



1995 to 2005 PE growth will average about 4% pa with LLDPE at about 8%

Metallocenes estimated to be 12% of PE market by 2005 (6 Mtes)

Gas phase technology is two thirds of new builds

There are substantial benefits for converters. A stronger product will allow further downgauging, i.e. thinner films. Superior processability means existing extrusion equipment can be used and output increased over LLDPE without processing aid. This is a significant product differentiation which the market will reward.

A further benefit of products produced from Innovene with INSITE catalyst technology is their outstanding sealability in packaging film. The seal starts to form at lower temperature and the hot tack strength is greater than LDPE, and even the best LLDPE. This is once again a result of regular distribution of branching in the polymer backbone, in this case short chain. The benefits will be faster packaging line speeds, e.g. in form-fill-seal applications.

While metallocene developments have to date been focused on speciality applications, the combination of INSITE and Innovene technologies will serve to extend their reach into the higher volume markets where the benefit of improved strength and processability is valued. Optical properties are also good and will enable broad market application in many packaging markets.

The aim is to achieve a neutral production cost position when compared with Ziegler-Natta operation which will enable market application to reach general purpose liners and sacks. Then, licensees will have the potential to upgrade their product slate with added value products which can substitute conventional LLDPE or LDPE.

The market

Growth of the world polyethylene market will average about 4 per cent per annum until 2005. The major producers will aim to capture as much of this opportunity as they can, so most new plant capacity will be to a swing design covering the highest growth segments LLDPE (9 mtes = 8.1 per cent per annum) and HDPE (8.2 mtes = 4.3 per cent per annum).

Today, metallocene products have achieved a very small share of this market but this is destined to change as the major gas-phase alliances drive down costs and deliver product performance for volume rather than niche applications. By 2005, metallocene products are estimated to take 12 per cent of the polyethylene market which represents 6 million tes produced by new build and retrofitted plants.

Opinions vary on how quickly metallocene products will impact on polyethylene markets. Furthermore, general conclusions that are made about Asia as a region, may not be applicable to specific countries since special factors often prevail. As an illustration, the size of the total Asian market is starting from a low level but increasing quickly at twice the level of GDP. All of the major countries have built, or have under construction, a significant amount of polyethylene capacity. However, the largest populations of China, India and Indonesia drive the investment almost exclusively for their domestic market which will reduce the immediate competitive need for metallocene products. For others, importers will reduce, even stop, and exports start, e.g. in Thailand, as supply exceeds demand towards the end of the century. In these cases, metallocene products can be a valuable addition to their range.

The earliest potential for metallocene products is likely to be in Japan and South Korea in order to re-establish a competitive edge. Less well-developed markets in terms of high-strength (C6/C8 LLDPE) film products, such as Malaysia may be slower to move to the new technology and will aim firstly for exports. In general, the order of market entry will probably relate to GDP per capita versus per capita PE consumption.

Chem Systems[1] have estimated the total metallocene and easy processing product market in Asia to be 1 million tes by the year 2000 and 3 million tes by 2005. The fastest and easiest route to the market will be to retrofit or drop in metallocene catalysts to existing plants.

This is the second key success factor. Asia is in a strong position having invested in 31 gas-phase plants which will total approximately 4 mtes polyethylene capacity by 1998. This represents 35 per cent of the PE capacity in the region.

Process technology

A typical polyethylene market in Asia is diverse and fragmented in its products and applications. It is usually characterized by the presence of HD film, tape and monofilament grades and LD per cent > LLD per cent.

Faced with this diversity and unpredictable demand patterns, especially in connection with exports to China, most Asian producers want technology capable of making all product types. Swing plants covering both HDPE and LLDPE are preferred to maintain high plant loading. In addition, the lowest investment and operating cost are often critical to selection and these are the reasons for gas-phase leadership.

The efficient removal of vast quantities of heat generated by ethylene polymerization in a world scale gas-phase reactor presents a significant technical challenge, especially as metallocene catalysts are highly active. The advent of breakthrough technologies such as **High Productivity** has met this challenge and single reactors are being designed now capable of making over 300 Ktpa of a full range of products. This increases economy of scale and cost competitiveness for licensees, the third key success factor.

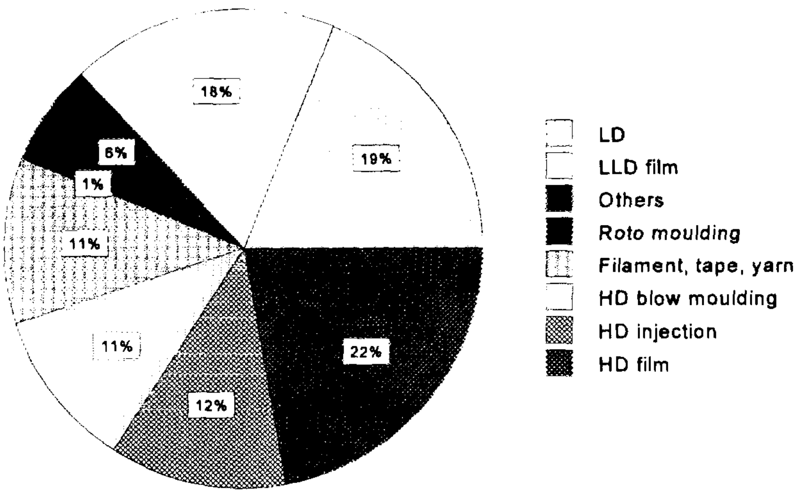
The way this is done is by injection of cooling liquid hydrocarbon directly into the fluidizing bed using a proprietary nozzle system. This modification is running in full commercial operation at both BP Chemicals Grangemouth and Lavera plants and increased capacity to the new design levels immediately on start-up.

Gas-phase technology has a broad or wide range of Melt Index (MI), density (915-970) and Molecular Weight Distribution (MWD). Solution phase gives excellent film products but only partial coverage of HDPE. It is precluded from high molecular weight, low MI blow moulding grades for large rigid containers because the polymer comes out of solution.

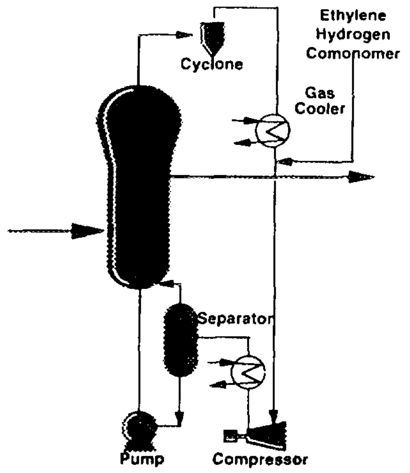
Older technologies cover a narrower product range and have higher operating costs. This is a major disadvantage for early entrants into domestic markets and those facing changing customer requirements.

The only area that gas phase does not reach today is the LDPE market. An LDPE look-alike is one of our primary product targets for gas-phase technology using metallocene catalysts since it is likely to be the product of most interest in Asia. There is a lot of LDPE consumed in Asia and producers face the decision either to replace old high-pressure plant or invest in gas phase with the capability of LLDPE and HDPE as well. Total substitution of LDPE capacity is perhaps unrealistic, but in a more export-oriented market, the added flexibility is a significant commercial advantage.

Typical Asian polyethylene market



Innovene process—high productivity

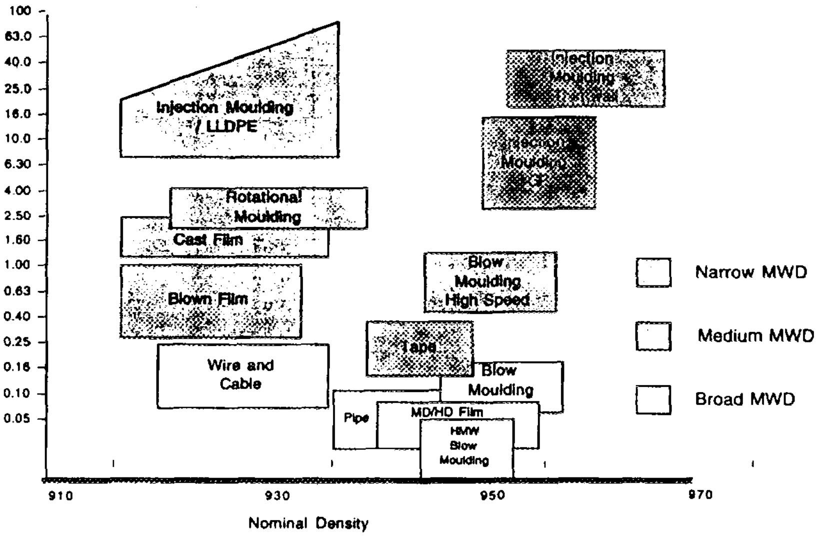


- Patent granted in US
- Single reactor capacity increase

1986 100 ktpa

1996 > 300 ktpa

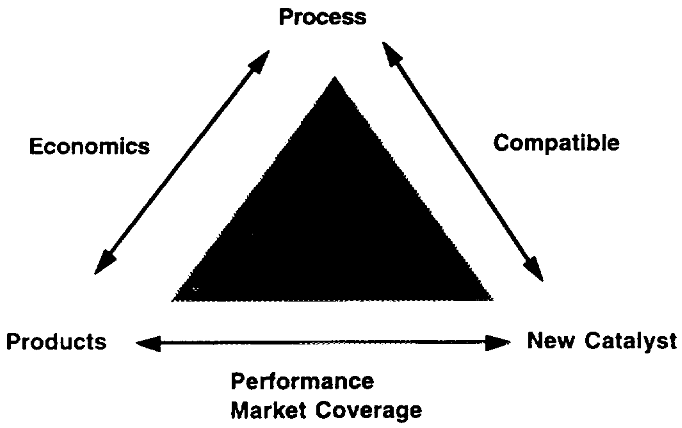
Product summary



PE technology application

Technology	Density Limits	Applications
High-pressure LDPE	<930	Film, injection moulding, wire and cable
Solution	>900-960	Film, injection moulding
HDPE slurry	>935	Blow moulding, pipe
Gas phase	>910-970	All major applications

Research and technology continuous improvement



BP/DOW technology vision

- **Single world-scale reactor with multicatalyst flexibility**

Advantages

- **Lowest cost**
- **Broadest product range**
- **New entry into LDPE and premium LLDPE markets**

The future

With gas-phase technology forecast to take 60 per cent to 70 per cent of new build capacity, it is set to become the industry standard in the region. It is essential for licensees that, having made substantial investments in world-scale plant that future catalysts are compatible with established Ziegler-Natta, chromium and metallocene types as well as the reactor hardware and conditions. This is the fourth key success factor. When this is achieved, the goal is to improve performance of products for converters and extend market coverage for the producer. In commodity sectors, there is a constant aim to drive down the costs of existing products.

The next target after high-strength, high-performance films and grades which reproduce the properties of LDPE is bimodal HDPE from a single reactor. Film is the main market with blow moulding and pipe to follow. This will require further development of a multi-functional Ziegler/metallocene catalyst.

Summary

A phased acceptance of high-performance metallocene products in the Asian market is anticipated after the four key success factors identified in this paper are met. In the medium to long term the market environment will become more demanding of differentiation and suppliers are positioning themselves to develop and deliver new technologies. In particular, metallocene product capability is required to ensure that the substantial investment already made in gas-phase polyethylene technology sustains its advantage and best fit with the Asian market. The key targets are an easily processed, strong LLDPE film and an LDPE look-alike which will penetrate the Asian market very quickly as soon as it is available.

Reference

1. PCI Plastics—World Polyethylene Supply/Demand Report 1994/95, November 1995
2. ChemSystems—The Global Polyolefins Industry: October 1996. A period of Structural and Technological Change

E. STRATEGIC BUSINESS ALLIANCES

Making moves with metallocenes

The wave in single-site catalysis is creating unlikely partners. The two leading US-based ventures—Union Carbide/Exxon Chemical and Dow Chemical/BP Chemicals are prominent examples of a new alliance strategy.

These alliances—and their number is growing—have similar characteristics. They nearly always combine the chemical division of a large oil company and a large pure-play commodity chemical company.

Each alliance marries a leading new catalyst technology with a major process licensing position. Without question, the leading developers of metallocene catalyst technology for polyethylene are Dow (INSITE) and Exxon (Exxpol). In regard to process licensing, Union Carbide is the No. 1 licensor of gas-phase polyethylene technology (Unipol I and II), and BP is the No. 2 licensor (Innovene).

There is a good reason to form alliances—namely to pay for the research effort that created single-site catalysts. It is estimated that total research costs by the four or five leading companies with the most metallocene patents have totalled well over $3 billion.

Exxon's metallocene catalysts offer Union Carbide and its Unipol gas-phase technology an expanded technology platform to work with.

The joint venture provides an attractive array of options for potential new licensees and the potential to sell retrofit packages to existing Unipol licensees and other gas- and solution-phase PE plants.

With over 150 patent families surrounding its metallocene catalysts, Exxon has been quietly leveraging its research position to build a global licensing foundation. It has a 50-50 alliance with DSM—Dex-Plastomers—for production of metallocene-catalysed PE at a 220-million-pound-per-year facility in Geleen, the Netherlands. Late last year, Borealis entered the European metallocene PE market by licensing Exxon's metallocene catalysts for use in Borealis's slurry loop PE process. Borealis expects to produce around 30,000 tons of metallocene-based materials in 1997 at its plant in Roenningen, Norway. Exxon is also expanding its Mont Belvieu, TX, linear low-density polyethylene (LLDPE) facility by 45 per cent to 839,000 tons to produce additional Exceed metallocene-LLDPE resins.

Dow's alliance with BP Chemicals is broadly similar to the Exxon/Union Carbide venture. It will focus on using the combination of Dow's INSITE technology and BP's gas-phase process—Innovene—to produce LLDPE. Gas-phase plants can be retrofitted to use Dow's INSITE technology.

Meanwhile, Dow is expanding its position in Thailand, with a 50-50 joint venture with Siam Cement PLC. The joint venture, Siam Polyethylene, will be the first Asian producer of metallocene PE outside of Japan. Dow is also licensing its INSITE technology to Asahi Chemical, which is converting a slurry PE plant to a 40,000-ton-per-year single-site catalyst-based HDPE plant in Mizushima, Japan. Production is slated to begin in the spring of 1998.

Asahi Chemical's new HDPE will be the first of its kind in Japan, although several Japanese producers have already entered the metallocene fray with metallocene LLDPE. With gas-phased metallocene technology licensed from Exxon, Mitsui and Sumitomo will jointly build a 200,000-ton-per-year plant in Chiba by the end of 1997, with the aim of beginning full-scale marketing of general purpose-grade metallocene LLDPE in 1998. Mitsubishi Chemical plans to convert its existing conventional LLDPE plant in Kashima to manufacture 200,000 tons per year of metallocene-based product by mid-1997. Mitsui and Ube Industries opened Japan's first metallocene LLDPE plant in 1995.

Other chemical companies are also developing new forms of catalyst technology. These include BF Goodrich, DuPont and Nova. Nova established a technology position in PE through its acquisition of DuPont's Sclair polyethylene technology.

The alliance between Union Carbide and Exxon is also significant because it resolves the patent dispute over the supercondensed mode technology developed by both companies. Now that the dispute is settled, polyethylene producers seeking to increase capacity are expressing greater interest in supercondensed mode technology. The technology can double a reactor's capacity at about one-half the cost required for a new plant.

Although a shakeout is one possibility, the more likely outcome is that the market will be carved up into high and low ends. Metallocene technology may not prove to be an all-embracing panacea. Companies such as Rexene can be every bit as competitive and meet their customers' needs with the traditional processes.

In any event, metallocene technology is designed to create more licensees with the ultimate goal of offering cheaper technology once the R&D costs are absorbed. (Source: *Chemical Market Reporter*, 17 March 1997)

Innovene and INSITE technology

Innovation in action to develop high-performance polyethylene technology

The Innovene process is being continuously improved by a research and technology team working at the leading edge of process and catalyst innovation. The aim is to make resins which: are cheaper to produce; convert to stronger end-products; are easier to process; and meet regional and worldwide market requirements.

A polyethylene grade that processes easily into a film product having very high strength is a particularly difficult combination to achieve. With conventional Ziegler and metallocene products there is a trade-off between strength and processability This is why the recently announced joint technical cooperation between BP Chemicals and the Dow Chemical Company is so significant. The Innovene process using INSITE catalyst from Dow is unique in its ability to achieve the required combination of strength and processability in its end-products.

Long chain branching

The reason for this break with convention is Dow's patented constrained geometry catalyst which polymerizes uniformly and selectively introduces long chain branching into a very narrow molecular weight distribution polymer chain. This is the only technology to successfully produce polymers with very narrow molecular weight distribution (MWD) and good processability. The products are stronger, but more processable, than LLDPE and, therefore, at a significant advantage over conventional Ziegler and high pressure LDPE technology based products. Very importantly, there is no need for expensive processing aids or to blend, and no need to change the extruder die when switching from LDPE.

The demonstration of no output penalty using existing extrusion equipment is key to wide acceptance in high volume markets. Innovene with INSITE is clearly differentiated in this respect and has already demonstrated an increase in output compared to LLDPE in tests at commercial scale. This benefit goes beyond "easy processing" LLDPE and could transform the polyolefins industry by expanding the current limits on polymer uniformity, performance, processability and versatility.

Homogeneous single site catalyst

Conventional linear low density polyethylene is produced by Ziegler-Natta catalyst with multiple active sites. Multiple active sites create polymers with varying molecular structures, resulting in variable distribution of the comonomer between polymer chains.

INSITE catalyst, in comparison, has only one active site. A single site tends to polymerize in a more uniform fashion, so that every molecule is similar—polymer chains are more consistent in length, and have more consistent incorporation of comonomer into the polymer—which results in a narrow molecular weight and comonomer distribution. This uniformity leads to exceptional, very predictable physical and mechanical properties. Both a narrow MWD and narrow comonomer distributions maximize critical performance properties such as toughness, sealability, clarity, and other properties important to product application. This is a distinguishing feature of INSITE constrained geometry catalyst technology.

Unique aspects of polymers protected by patents

The polymers are so unique that Dow sought and received a composition of matter patent from the US Patent and Trademark Office. Such patents are rare. Only one was issued in 1992 involving single site technology: the patent issued to Dow.

The Patent Office obviously recognized the unique aspects of polymers produced via INSITE technology—that they offer all the performance advantages expected from single-site catalyst resins, plus superior processability due to their long chain branching on a linear structure.

A break from tradition

Innovene with INSITE is aiming to open doors to many applications and improved cost-performance options, for example, the opportunity of high-performance and cost-efficient products for applications ranging from packaging film, extrusion coating wire and cable, and other consumer and industrial goods.

Complementary process technology

The efficient removal of vast quantities of heat-generated by ethylene polymerization in a world-scale gas-phase reactor presents a significant technical challenge especially with the latest generation of catalysts. Modification of the reaction loop by addition of a liquid separation and proprietary injection system (High Productivity) was a breakthrough that met this challenge and has enabled single reactors to be designed capable of making over 300 kilo tons per annum of a full range of products. The potential of the technology was rapidly demonstrated on two world- scale Innovene units in Europe with immediate increase in production to new design capacities. The team who made the major breakthrough received the BP Chemicals 1996 Gold Innovation Award, and a patent (US 5,541,270) for the technology was recently granted in the USA.

Innovene is a registered trademark of The British Petroleum Company.

INSITE and Dow are registered trademarks of The Dow Chemical Company.

For further information, contact: John R. F. Steedman, Licensing Area Manager, BP Chemicals, Pinners Hall, 105-108 Old Broad Street, London EC2N 1ER, UK. Tel.: +44 (0) 171 496 2842; Fax: +44 (0) 171 496 2897; e-mail: steedmjr@bp.com.

Polyethylene—fighting for technological supremacy

Exxon Chemical and Union Carbide are to form a joint venture to develop and license their metallocene and process technologies for making polyethylene. Their agreement comes hot on the heels of a similar deal involving BP Chemicals and Dow Chemicals.

The Exxon/Carbide agreement follows a year of discussions. It takes in Carbide's Unipol gas-phase processes and catalysts, and Exxon's EXXPOL metallocene catalysts and supercondensed mode technology gas phase process improvement. The companies say that the venture resolves current and "likely future" legal disputes over ownership of the technologies. The joint venture will have clear ownership and can place its full energy towards development and sale of the superior technologies to polyethylene producers.

The venture, which should start operating by the end of the year, will offer a "portfolio of advanced technologies" for new and existing polyethylene plants. It will also make and sell metallocene catalysts for polyethylene production.

The initial focus of the new company will be metallocene-catalysed linear low-density polyethylene (LLDPE). The companies quote industry experts' predictions that more than half of all LLDPE—which has a growth rate of 7.2 per cent per annum—will be made using metallocenes by 2005. They add that metallocene plastics will also replace products made from other plastics and start to take over from metal, glass and paper in packaging applications.

A week earlier BP and Dow unveiled a technology agreement, matching BP's gas-phase manufacturing process Innovene with Dow's INSITE metallocene catalyst. They claim that the two together should produce better polymers more efficiently.

The two companies have been working on how to combine Innovene with INSITE since the middle of 1995. They say that they have successfully demonstrated in BP's pilot plant that the two technologies can produce high-performance polymers with better processability and impact strength, and heat seal and optical properties. Products should be ready for commercial delivery by 1997.

As well as improved performance characteristics, the partners are hoping for better production economics, easier processability during converting, potential for new applications, low-density polyethylene (LDPE) look-alike grades, high-strength LLDPE films and easy processing LLDPE.

LLDPE for commodity markets is one of the major targets for BP and Dow as well as Carbide and Exxon; according to BP's figures, it is growing at 8 per cent per annum.

BP and Dow are expecting the polyethylene market to grow by 4 per cent per annum up to the year 2000, according to 12 per cent of this market. Gas-phase technology already accounts for two thirds of new reactors.

Licensees will not have to invest in new facilities, but will be able to adapt their existing gas-phase reactors. According to BP, the only changes will be the amount of catalyst and the composition of the gas in the reactor.

So why this sudden spate of technology collaborations? Companies are moving closer together. They want to fill in technology gaps and survive in a scientifically complex area and highly competitive market.

There is a general feeling that metallocenes will succeed in getting a strong market position, but there are other technologies which are still very viable and have been proved. BASF, DSM and Montell also have very strong technologies, involving different processes. (Source: *Chemistry & Industry*, 19 August 1996)

Polypropylene—Dow enlists Montell's know-how

Dow Chemical was expected to enter the polypropylene business in the autumn of 1996. It plans to become one of the top global suppliers over the next 10 years by licensing technology from Montell and developing metallocene catalysts.

Dow will license Montell's Spheripol polypropylene process technology for an undisclosed sum. The polypropylene market is worth $22 billion, with a growth rate of 5 per cent per year. Dow hopes for eventual sales of $1 billion.

The company is pinning much of its hope for success on metallocene chemistry. Metallocene catalysts will expand the range of polypropylene's uses, building new demand and further supporting the above-average growth rates in the marketplace.

Dow will use Spheripol technology at a new 200,000 tons per annum plant to be built in Schkopau, Germany; start-up is scheduled for early 1998.

By the year 2000, the company plans to construct at least two other manufacturing plants. It is looking at sites in Tarragona, Spain, the US and in the Pacific region.

However, the company expected to start selling polypropylene made by Montell by the fourth quarter of 1996. Under the agreement, both companies will sell and buy products from each other.

Formed in April 1996, Montell is a joint venture between Montedison and Shell. It boasts 20 per cent of global polypropylene sales. (Source: *Chemistry & Industry*, 17 June 1996)

Metallocene patents deal for Hoechst/Fina

Hoechst and Fina have finalized a joint agreement on cross-licensing of patents in the field of metallocene catalysts for polyolefin manufacturing.

Under the terms of the agreement Hoechst will have worldwide rights to use Fina for both its own polyolefin business and its metallocene catalysts businesses.

Fina will have worldwide rights to use Hoechst patents in its own polyolefin businesses.

The arrangement is non-exclusive except in the area of syndiotactic polypropylene and cyclo-olefin copolymers.

The agreement also provides for rights for Hoechst under Fina patents to manufacture metallocene catalysts for its customers.

The agreement also allows for the possibility of a future supply by Hoechst of Fina-developed metallocene catalyst to Fina. (Source: *European Chemical News*, 28 April-4 May 1997)

F. NEW APPLICATIONS

Metallocene compounds debut at medical show

In another development, new federal standards could ease rigorous rules used before new medical products can be introduced.

Metallocene polymers debuted in new medical applications at the Medical Design & Manufacturing (MD&M) Exposition in Anaheim, CA, amid increasing signs that the US Food and Drug Administration is significantly easing the burden required to introduce new medical devices in the United States.

Dow Plastics, Midland, MI, displayed collection bags and pouches made from Affinity polyolefin plastomer resins. They are said to offer similar performance to bags made from polyvinyl chloride, but are lighter weight due to a lower density. Because of the inherent strength of the metallocene resins, the new bags can be downgauged 30 per cent.

Dow said the products can be recycled and incinerated safely, even in older facilities. In addition, Plastics Welding Technology of Indianapolis has demonstrated that existing RF sealing equipment, with supplemental technology, can produce strong welds on materials such as polyolefins which previously could not be sealed with this method.

Exxon Chemical, Houston, introduced blends of Exact 3024 metallocene plastomer and Escorene polypropylene (PP) that produce clear plastics described as resistant to embrittlement after irradiation, resistant to softening at elevated temperatures and remain very white even after irradiation.

Blends containing as little as 7.5 per cent to 12.5 per cent of Exact can be used in devices that are radiation sterilized at commonly used doses. Increased loadings of the plastomer further improve the resistance of PP to embrittlement following radiation. Unlike conventionally produced polyethylene, the plastomer, which is described as an ultra-low density ethylene polymer, causes only a negligible increase in haze when blended with PP.

GLS Corp., Cary, IL introduced a new extrudable grade of super-soft thermoplastic rubber compound with a hardness of 15 Shore A that is primarily based on new polyolefin plastomers. This compound now gives design engineers the ability to design flexible profiles that are softer than ever obtainable with existing technologies other than foamed materials. The material is said to possess excellent clarity, and an ultimate elongation greater than 400 per cent. It is gamma sterilizable and can be foamed. (Source: *Plastics World*, March 1996)

Nova, Dow give PE a boost

Nova Chemicals Ltd. in Calgary, Alberta, found its competitive response to metallocenes when it bought the SclairTech solution polyethylene (PE) process and a nearly 40-year old solution reactor plant in Sarnia, Ontario, from DuPont Co., Wilmington.

Nova's PE group has since then developed an advanced series of SclairTech reactors, involving a breakthrough in high-intensity mixing and agitation plus reactor configuration. Then this is used with new advanced, high-efficiency Ziegler-Natta catalyst developed for the multi-reactor configuration, to make octene-copolymer linear low (LLDPE) that outperforms metallocenes above 0.905 density.

Nova is confident enough of its new process to be planning the first commercial-scale plant to use the new high-intensity, supercharged Sclair process, a 770-million-lb/year reactor series to be built in Joffre, Alberta, tentatively scheduled for start-up in the year 2000 (pending board approval). A decision on the plant is expected soon.

Start-up is timed for the completion of a new ethylene cracker, being built as a joint venture between Nova and Union Carbide Corp., Danbury, CT. The new materials will address both speciality and commodity grades. Applications include thin-walled injection moulding, speciality modified atmosphere films for meat packaging, coatings and speciality tapes.

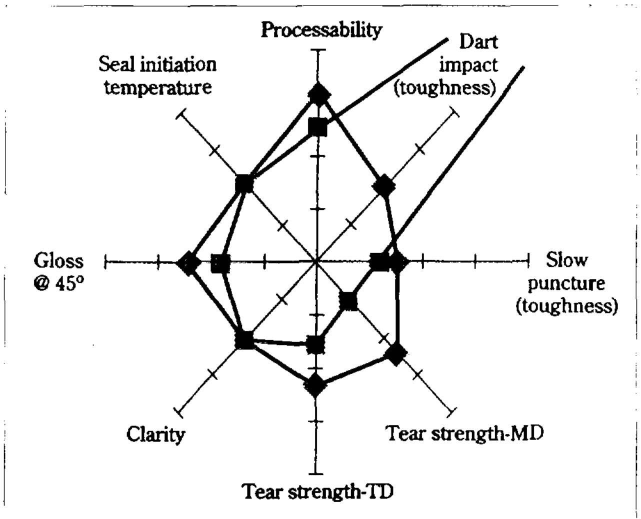
Solution reactors lend themselves to density tailoring by modifying reactor conditions (notably temperature and feedstock composition) without catalyst change and to very efficient product turns when catalyst is changed over. Nova said that while its enhanced multi-reactor process can use metallocene catalyst, it plans instead to employ a new advanced, high-efficiency Ziegler-Natta catalyst to make a bimodal material with relatively narrow molecular weight distribution, eliminating both very short and very long molecular weight tails. This achieves a combination of improved toughness and optics that matches metallocene-PE properties everywhere except Dart impact, according to the company.

Dow's mPEs

Dow Chemical Co., Midland, MI, meantime, in December 1996, made the first commercial-scale runs of its new enhanced PE using INSITE catalyst, when it started up a converted 440-million-lb/year solution reactor in Plaquamine, LA, modified to run Insite catalyst. The start-up made first conventional Dowlex LLDPE with Ziegler-Natta catalyst, then Affinity metallocene PE with Insite metallocene catalyst, and finally commercial quantities of six new grades of enhanced PE, also with INSITE catalyst.

The first six enhanced grades have greater than 0.920 density. They target industrial and consumer cast and blown film; food and speciality packaging film; injection and rotomoulded articles; extruded sheet; and profiles, Dow said. Actual grades and properties are expected to be announced, along with a new trademark, in the first quarter. Dow said it does not intend the new PE to cannibalize strong sales of Dowlex resins, but to capitalize on greatly improved Dart impact properties and a broader window for improving flexural modulus. (Source: *Plastics World*, January 1997)

Properties of Nova's new Ziegler-catalyst Sclairtech octene LL vs. metallocene-made hexene LL



Source: Nova Chemical

Metallocene grades offer improved clarity, toughness

Evidence that metallocene-based polypropylene grades offer strong performance benefits in thinwall, transparent moulded packaging and other mouldings is being offered by BASF AG, Ludwigshafen, Germany. Specifically, the supplier says trial runs of its commercial M Novolen metallocene PP (mPP) grades demonstrate improved toughness, reduced cycle times, and a notable step up the ladder of clarity versus conventional PP grades.

In view of its unique balance of properties, mPP will be a challenger in applications that until now have been the preserve of "traditional" transparent thermotplastics, according to BASF.

The improved clarity of mPPs puts them in contention versus higher-priced polyethylene terephthalate resins and styrenic-based blends in high-clarity applications, especially frozen and other thinwall food packaging, disposable drink cups, and large housewares. The mPPs reportedly work well as drop-in replacements for PP, using the same tools and with only minor changes in processing conditions.

BASF says the most meaningful way to judge mPP is to compare its properties to those of the best available PPs.

The PP suppliers' trials thus compare mPP with its latest-generation, high-crystallinity and nucleated versions of PP.

BASF tests show homopolymer mPP offering transparency of 93 per cent (i.e., 7 per cent haze). This compares with 47 per cent transparency for high-crystallinity PP. It is also claimed to outperform new clarified, nucleated products (89 per cent clarity).

A random copolymer mPP, meanwhile, is said to achieve a 96 per cent transparency rate. BASF claims this is the best clarity result ever obtained with PP.

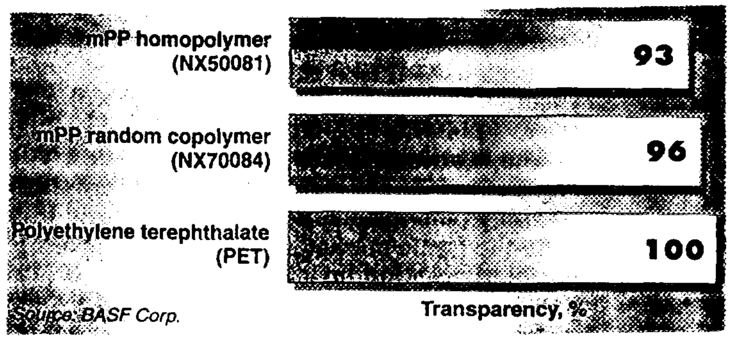
In trials with large moulded housewares, BASF found homopolymer and random copolymer mPPs were relatively easy drop-ins when replacing conventional random copolymer. What favours mPP in this application are a 10 per cent reduction in plasticization times, 50 per cent lower injection pressure, and improvements in clarity and surface properties.

A major payoff for mPP in thinwall moulded containers is reduced cycles. This is tied to the resin's ability to deliver a given level of toughness and stiffness, while achieving a higher than conventional melt-flow rate. A 60-MFR product offers 10 per cent faster cycle time than a nucleated grade, with comparable clarity and gloss.

Alternatively, the high-flow mPP was able to match the cycle-time performance of a high-crystallinity PP in thinwall containers, while offering significantly higher clarity and gloss.

Transparent disposable drinking cups are often moulded from styrenic blends and alloys that enhance clarity. BASF trials, using an original styrenics mould, show a 60-MFR mPP can significantly improve brittle failure performance versus the styrenic cups, while achieving about equal clarity and appearance. The downside is some loss of wall stiffness. (Source: *Modern Plastics International*, March 1997)

Metallocene PP approaches the transparency level of PET



Source: BASF Corp.

G. COMPANY NEWS

Metallocenes—Overview

Metallocene technology is no longer regarded as being simply a wave of the future following a number of recent launches of metallocene-based polymers. Although the improved performance characteristics of metallocene polymers are widely acknowledged, processors and packagers still have major concerns over cost, processability and the difficulty of obtaining supplies.

The ability of metallocene catalysts to produce polymers with a "tight" molecular weight distribution, and with the regular insertion of monomers and comonomers, has led some people to talk of metallocenes as creating a revolution in the industry.

At the Metallocenes Europe '97 conference in Düsseldorf, the penetration of metallocenes into the plastics industry was acknowledged with presentations by five companies with semi-commercial or commercial production of metallocene polymers. Chief among these were Dow Chemical and Exxon Chemical, who have both recently announced the production of metallocene polymers on a large scale.

Dow is producing its *Elite* polyethylenes at its Plaquemine plant in Louisiana with an initial capacity of 200,000 tons/year. Future plans call for an additional 210,000 tons/year at a European site by the first quarter of 1998. No site has been selected, although it is believed that BSL's site in Germany could be a possible contender for either a new or retrofit plant. There are also plans for an additional 250,000 ton/year capacity by the end of 1998 at Dow Chemical's Sakastchewan facility in Canada.

Meanwhile, Exxon Chemical is producing metallocene-based LLDPE at 110, 000 tons/year at Mont Belvieu, TX, and converting its Cipen joint venture polyethylene facility at Notre Dame de Gravenchon.

The dominance of the patent position in metallocenes by a few producers has led a number of companies to develop other single-site catalysts.

Tosoh has produced phosphametallocene-based catalysts for ethylene, propylene and styrene polymerizations. These homogenous phosphametallocene-based catalysts have a similar framework to metallocene catalysts, but have a special phospholyl anion ligand.

The structure consists of a zirconium-based organometallic complex and is said to offer improved proccessability, high activity and broader molecular weight distribution polymers than are possible with conventional metallocenes.

Hoechst is working on a new class of catalysts described as C_1-symetric single-site catalysts. The system is a tertrahydroidenyl-based metallocene where the second cyclopentadienyl is connected to the 4-position. This produces a catalyst with a more tightly constrained catalytic site. The rigid and constrained backbone opens the bent metallocene wedge, resulting in a change of steric and electronic properties at the transition metal centres. The new catalyst system is being developed at the laboratory-scale and so far it has been used to produce homo- and copolymers of ethylene and propylene.

Recent developments in the technology have also been driven by the need to lower the cost of catalyst andcocatalyst production, and to address the problem of processability.

One area of concern is the high cost of the metallocene catalysts and cocatalysts. Most industry observers generally agree that the price of metallocene-based polymers must not be higher than their conventional counterparts in order to achieve significant market penetration.

Estimates show that current world output of metallocenes is only around the 10 ton/year mark. This is one of the reasons that metallocene catalysts can cost in the region of thousands of dollars per kilogram—quite a lot more than the $50/kg which the petrochemical industry is used to spending on catalysts. Not only do metallocenes require lengthy multi-step synthesis, but they also require special handling, being especially sensitive to moisture and air. Although metallocene catalysts show extraordinary productivities in relation to chromium catalysts, this does not compensate for their high cost.

The methyl aluminoxane (MAO) cocatalysts used to activate metallocene catalysts also represent a major expense in their use as well as producing handling difficulties within the reactor.

Akzo Nobel recently introduced modified methyl aluminoxanes which it claims have improved performance. The PMAO-IP (polymethyl aluminoxane-improved performance) has increased solution stability and a higher activity when used in ethylene slurry polymerization tests. A number of modified MAOs (MMAO-3A and MMAO-7), and an SMAO (silica-supported MAO) have also been introduced.

BASF has produced a supported catalyst system which replaces the MAO with boron cocatalysts. The process has already been successfully run in both slurry and fluidized bed pilot plants at Ludwigshafen, Germany. It can also be applied to gas-phase reactors. BASF claims that the system can be described as a "drop-in" catalyst in existing processes and says the system produces no reactor fouling. The system has so far been successfully used to produce BASF's *Luflexen* polyethylene in a slurry loop pilot-plant reactor. The key to the system is an efficient way of depositing the metallocene and cocatalyst on a silica support.

Observers will be watching the progress of Nova Chemicals' advanced *Sclairtech* solution for LLDPE with interest. The multi-reactor technology is capable of being operated in a 350,000 ton/year single train plant. The process uses a proprietary Ziegler-Natta catalyst which produces a narrow molecular weight distribution. The use of multiple reactors is claimed by Nova to make a product which is easy to process and has a good balance of properties.

The advanced *Sclairtech* process was originally developed from technology acquired from DuPont. The reactors are able to make a product with a defined molecular weight because Nova has focused its research on creating a homogeneous environment within the reactor. This is an element of the process which many companies neglect in favour of catalyst development.

A metallocene polymer may have exceptional dart impact properties, but in practical situations you are more likely to have a child pushing its finger through a plastic packaging than someone firing a dart at high velocity (the measure of dart impact) at it. The tremendous increases in some aspects of performance achieved by metallocene polymers may not be such a desirable property in practice.

Although a number of processors and packaging companies are beginning to systematically develop metallocene polymer products, progress has been inhibited by the problems of poor processability and lack of availability of metallocene polymer, with one processor describing metallocene polypropylene as a mythical beast. However, these problems could be about to end as more and more commercial quantities of metallocene polymers come on stream.

There is a learning curve which processors and packagers must go through to bring metallocene products to the marketplace. In an industry where margins are traditionally tight, there is an unwillingness to take equipment off line to test the new polymers. However, there are many in the industry who are aware of the potential of metallocene polymers and are willing to do the hard work necessary to develop the technology. The use of metallocene polymers at a blend of between 10-30 per cent in the plastic is being recognized as the best way to key in its useful properties while minimizing processing problems.

The superior properties of metallocene polymers, such as improved organoleptic, optical and strength qualities will drive their use in special applications such as food and pharmaceuticals packagings. However, there is a saying in the packaging industry—"the best technical performance is price". (Source: *European Chemical News*, 21-27 April 1997)

BP product summary

The Innovene process from BP offers a low-cost and flexible way to produce a wide range of LLDPE, MDPE and HDPE products to meet the changing demands of the polyethylene markets around the world.

LLDPE products are used in a wide range of film, injection moulding, rotational moulding and extrusion applications. The LLDPE products have excellent mechanical properties, are virtually gel-free and are available in a range of grades using butene, hexene and 4 methyl pentene-1 as comononers.

The narrow molecular weight HDPE products are recognized for their superior quality in injection moulding applications. The broad molecular weight HDPE products offer a new competitive alternative for blow moulding, pipe, film and other extrusion applications.

Products from the Innovene process are produced by BP Chemicals and licensees of the process in many countries around the world. These products are sold under a variety of names, including Innovex®, Rigidex®, Petrothene, Indothene and many more.

A selection of the products available from the Innovene process is described below.

Film market

The BP Chemicals LLDPE and HDPE film grades cover the full range of applications and technologies in the film industry. By comparison with solution and slurry processes, Innovene provides the widest range of melt indices and densities.

LLDPE film

BP Chemicals has developed an extensive grade range based on butene as the comonomer and also on hexene or 4MP1 for the production of copolymers with enhanced performance.

Films produced with BP Chemicals resins have the following benefits:

- Gel-free and excellent optical properties;
- High-impact performance;
- High tear strength;
- Excellent sealability.

The superior mechanical properties of LLDPE grades over LDPE grades allow significant down-gauging potential. This has resulted in very high growth rates for LLDPE, and grades from the Innovene process are now used worldwide.

HDPE/MDPE film

The production of very thin gauge carrier bags (10 to 15 micron) requires polyethylene grades with very high tensile strength and easy processing. BP Chemicals has developed an HDPE/MDPE grade range offering the optimal combination of processability (bubble stability) and mechanical properties (impact, tensile and tear strength) for this market.

HDPE Blow Film

Product	Density	HLMI (21.6 kg)	Applications
HD 5301-4 FB	953	9	Very thin strong film, carrier bags
HD 4602 FB	947	15	Carrier bags, trash bags
HD 3802 EA	938	14	Shopping bag, blending component

Test methods used: Density ISO 1872—1986/ISO 1183D
Melt—Index ISO 1133

Blow moulding market

BP Chemicals has over 30 years' marketing experience of broad molecular weight distribution HDPE for blow moulding applications.

This in-depth knowledge of market requirements has assisted the research and development of resins from the Innovene process.

Now, licensees have the capacity to control molecular weight distribution from medium broad to very broad depending on the end application.

As a result BP Chemicals has been able to develop its blow moulding grades from the Innovene process with:

- An exceptional combination of stiffness/stress-cracking performance;
- Processability under standard machine settings.

These benefits hold the key to the evolution of the detergent, household and industrial chemical bottles market.

Under marketing and ecological pressure, lightweight bottles for concentrated detergents are in demand. Only HDPE blow moulding resins offering an enhanced stress-cracking resistance can meet this requirement.

Furthermore, the enhanced stress-cracking performance of BP Chemicals grades allows their use in blends or co-extrusion with recycle materials. The end-product is then strong enough to meet the required market performance.

A high molecular weight grade range is also available for the production of containers, drums and IBCs from 5 to 2,000 litres.

BP Chemicals has acquired a market-leading position with its full range of Innovene resins for injection moulding applications.

The unique molecular weight distribution of BP Chemicals grades enables:

- Easy and fast processing;
- Outstanding mechanical properties;
- Excellent environmental stress-crack resistance.

Injection moulding market

BP Chemicals grades are widely used in crates, pails, dustbins and houseware applications. Furthermore, they are the preferred resins for food contact applications or medical use since they better the most stringent requirements for odour and taste.

BP Chemicals resins have a good reputation in the market for consistency. This is an attribute of the catalyst's ability to control molecular weigh distribution over the product range. Converters find this quality especially beneficial because consistency minimizes both changes to machine regulation during processing and the generation of scrap.

Many moulded products are for outdoor use and therefore require UV protection. BP Chemicals has developed several grades with specific additives packages in order to maximize the UV resistance at the lowest possible cost.

Pipe market

BP Chemicals has more than 25 years experience in selling resins into the gas and water pipe markets. As a result, we understand the exacting standards that must be achieved by resins and compounds in order to satisfy the sophisticated market needs.

With this experience, BP Chemicals has been able to develop Innovene MDPE and HDPE grades which meet the gas pipe and water pipe markets' requirements.

The grades which have been developed have high resistance to:

- Hydrostatic pressure;
- Fracture propagation;
- Creep;
- Environmental stress-cracking.

BP Chemicals has developed black and yellow compounds on an industrial scale to meet not only international standards ISO and PPI, but also the much more demanding requirements of European end-users.

BP Chemicals has also developed grades for other pipe applications such as irrigation drip or ducting pipes.

Rotational moulding market

For many years, BP Chemicals has been a leading supplier of rotational moulding resins in Europe, sourcing all its requirements from its Innovene plants at Lavera, France.

The flexibility of the Innovene process, combined with the unique molecular weight distribution of BP Chemicals grades and stabilization package optimization, has allowed the development of products offering:

- Optimum impact and stress-cracking resistance;
- Excellent processability with short oven residence time;
- Easy mould release;
- Good weathering properties.

BP Chemicals grade range covers 95 per cent of the market requirements.

Tape and monofilament market

Demand for products capable of making woven sacks, netting and other knitted fabrics has traditionally been met by polypropylene. In some markets, especially Asia, polyethylene is now used for its improved weatherability, chemical resistance and softness.

An HDPE grade has been developed for the Asian market offering:

- Excellent processability due to the absence of gels, thus avoiding breakage during processing;
- High tenacity.

In addition, BP Chemicals can advise licensees how to reduce tape fibrilation and wearing during processing.

Wire and cable market

Telecommunications: BP Chemicals has developed LLDPE and MDPE products with a broad molecular weight distribution for the telecom market.

Compounds made with these grades offer:

- Same processing as LDPE on conventional machinery;
- Superior environmental stress-crack resistance;
- Excellent mechanical resistance at low temperature.

The electricity industry has traditionally used LDPE for power cable insulation. However, low voltage cable can be insulated by a cross-linked LLDPE layer.

Innovene products made with Ziegler catalyst can be used for the production of silane cross-linkable compounds for power cable insulation.

Extrusion coating market

The extrusion coating market is traditionally LDPE-based due to its advantage regarding neck-in effect and draw resonance. However, for some applications such as photographic paper, HDPE is added to LDPE in order to enhance the abrasion resistance of the polyethylene layer for better paper quality.

The ability of the Innovene process to produce gel-free products has allowed the development of HD 6070 FA which meets the key market requirements of high optical properties and easy processing.

For more information contact: J.R.F. Steedman, BP Chemicals, Penners Hall, 105-108 Old Broad Street, London EC2N 1ER, UK. Fax: +44 171 496 2897.

Rotomoulding

Product	Density	MFR 2.16 kg	Applications
HD 3840 EA	938	4.0	Septic tanks, silos, general tanks and containers
HD 3840 UA	938	4.0	UV stabilized version
HD 3560 EA	935	6.0	Toys, technical items, baby seats
HD 3560 UA	935	6.0	UV stabilized version
HD 2840 EA	928	4.0	IBC, chemical tanks
HD 2840 UA	928	4.0	UV stabilized version

Key	Additive package
EA:	Neutralizer, antioxidant
UA:	Neutralizer, antioxidant, UV stabilizer

Test methods used: Density ISO 1872—1986/ISO 1183D
Melt—index ISO 1133

Tapes and monofilaments

Product	Density	MFR 2.16 kg	Applications
HD 5710 AA	957	0.9	Knitted sacks, woven covers, nets, ropes, geomembranes
HD 5710 UV	957	0.9	UV stabilized version

Test methods used: Density ISO 1872—1986/ISO 1183D
Melt—Index ISO 1133

Wire and cable

Product	Density	MFR 2.16 kg	Applications
LL 2406 AA	924	0.6	LLDPE jacketing
HD 4002 EX (*)	940	0.15	MDPE jacketing
HD 3506 EX (*)	935	0.6	MDPE insulation grade
HD 2840 EA	928	4.0	Low voltage power cable insulation
HD 3840 EA	938	4.0	Low voltage power cable insulation

(*) Not commercialized

Test methods used: Density ISO 1872—1986/ISO 1183D
Melt—index ISO 1133

Extrusion coating

Product	Density	MFR 2.16 kg	Applications
HD 6070 FA	960	7.6	Extrusion coating photographic paper

Test methods used: Density ISO 1872—1986/ISO 1183D
Melt—index ISO 1133

(Source: *BP Product Summary, BP Chemicals*)

High productivity using Innovene gas-phase technology

BP Chemicals proprietary **High Productivity** technology is a major breakthrough in polymerization. The result of extensive development, it opens up a new era for polymer producers. The benefits are extensive and are now available to both new and existing licensees.

The benefits of High Productivity technology are more than a 100 per cent increase in output from a single reactor; up to a 50 per cent reduction in investment costs for new plants; simply retrofitted into existing reactors; optimum process for "next generation" catalyst systems such as metallocenes.

High Productivity, combined with the superior process and product performance of the BP Fluid Bed Process, is the world's leading polymer technology.

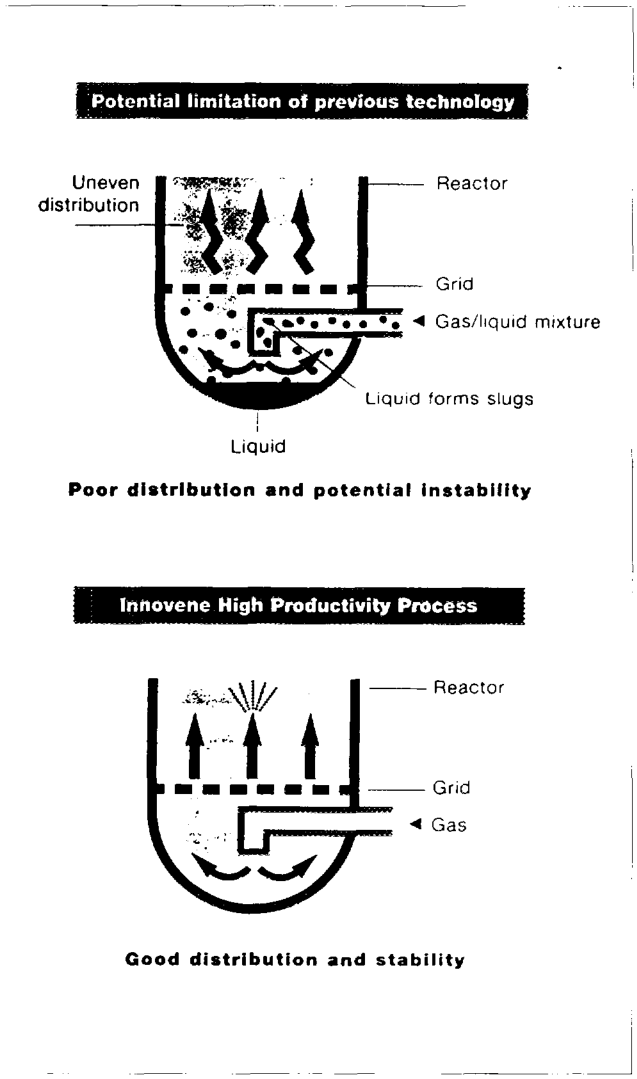
Previous forms of gas-phase technology which return a mixture of gas and liquid into the reactor are limited by the maximum amount of liquid which can be held in the gas stream. The limit is reached when an overload of liquid occurs. This consequently restricts heat removal from the fluidized bed and may cause instability in operation.

In the BP Chemicals High Productivity process, this limitation is overcome by separating the liquid from the gas stream. Proprietary nozzle technology is used to inject the liquid directly into the fluidized bed.

These innovations have several important technical advantages, such as optimum distribution and vaporization of the liquid in the fluidized bed; the highest heat removal capacity of any gas-phase technology; and the ability to disperse catalysts and modifiers with the liquid to the interior of the fluidized bed.

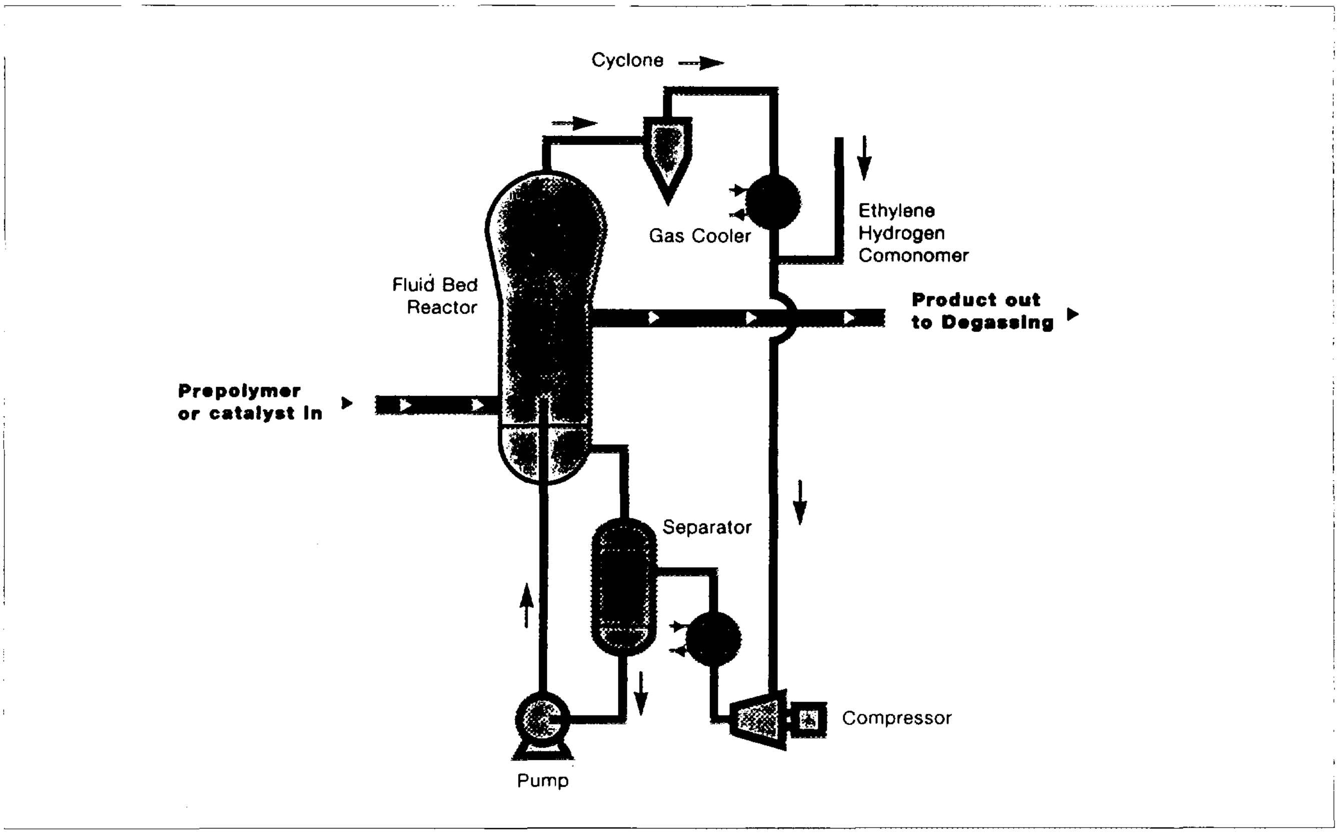
These advantages combine to maximize the productivity of the reactor, and may be applied equally to both existing catalysts and "next generation" catalysts such as metallocenes.

Figure 1. Diagram showing the effects of excess liquid in previous technology compared with High Productivity



The core of the existing fluid bed process remains unchanged. The simple addition of a liquid separation and injection system are all that is required. Process improvement packages are available for existing gas-phase licensees and the technology is also available now to all new licensees.

Figure 2. Innovene High Productivity technology applied to the BP Fluid Bed Process



Innovene innovation by BP Chemicals

Over 200 technologists are employed in the BP Chemicals Research Centre at Lavéra, France, which specializes in the development of the BP Fluid Bed Process. The development of the **High Productivity** process was completed using the extensive resources of this centre in conjunction with technologists from the BP Chemicals Licensing Business and specialists from the BP Group Research Centre at Sunbury.

The technology has undergone extensive testing using the most advanced facilities in the world for the development of fluidized bed technology. The unique BP Chemicals X-Ray Imaging Facility was used to prove the initial design of the system. A range of scale-up facilities from a bench scale reactor through continuous pilot plants to a three-metre diameter commercial reactor were available to the development team.

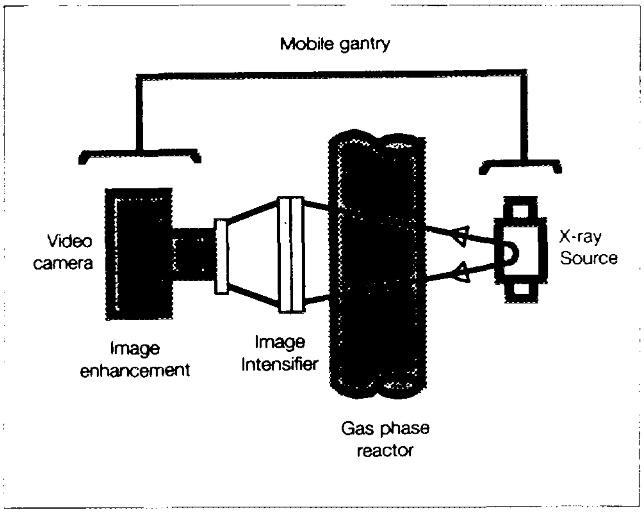
Commercial products from the process were tested successfully against the demands of the global market using the wide range of application equipment owned by BP Chemicals.

The unique, state-of-the-art BP Chemicals X-Ray Imaging Facility has made an essential contribution to the successful development of High Productivity technology.

The X-Ray Imaging Facility enables complex fluid-dynamic flow patterns within large-scale test reactors to be captured on video for analysis. The facility provides real-time moving images of the internal flow patterns of gases, liquids and solids within the fluidized bed operating under realistic process conditions.

The technique gives the BP designer an unrivalled insight into the fluid dynamics within the bed. In the case of the High Productivity process, the depth of penetration of the liquid from the injection nozzle can actually be seen. This facility enables different nozzle designs to be optimized and "new generation" catalysts to be observed prior to their use on a commercial scale.

Figure 3. X-ray imaging



Near-pure hexene-1 from Phillips Chemical

Phillips Chemical plans to commercialize a new catalyst to produce hexene-1, the comonomer used in HDPE and LLDPE production. The ethylene-based process is claimed to produce hexene-1 quickly and simply at a purity of 90-95 per cent, higher than other processes currently provide. The company has also developed a new generation catalyst that removes acetylene from ethylene streams and converts it into ethylene. Acetylene can destroy the effectiveness of PE catalysts if not removed.

The developments were revealed at a press conference recently when Phillips announced it was entering the LLDPE film market with a metallocene catalyst-based version (mLLDPE). Phillips has produced several million pounds of mLLDPE using its metallocene catalyst on a commercial-scale reactor at its Houston complex for trials at several select customers.

Phillips scientists have compared properties of conventional LLDPE with its metallocene-based mLLDPE. While tear properties are comparable, mLLDPE has superior dart impact toughness, excellent clarity, high gloss and low extractables. The resins, with a 0.920 g/cm^3 density, will be aimed initially at film packaging applications and can be processed on current equipment. Experiments on other grades have been carried out in pilot and developmental plants.

The catalyst requires minimal process changes to its slurry loop process, keeping costs down, said Phillips. The slurry loop reactor's good heat transfer characteristics are claimed to be a major design benefit for using metallocene catalysts. The process can dissipate heat from high productivity catalysts at high reactor throughput.

Other features of the reactor design with metallocene catalysts are clean running with no fouling of heat exchanger surfaces. As small amounts of catalyst must be added continuously, the reactor provides uniform catalyst feed for proper mixing and reaction. Production of fluff particles (fines) is reduced and the fluff particles that are produced are uniform in size. (Source: *European Chemical News*, 10-16 March 1997)

Exxon adapts metallocene catalysts for slurry PE process

Exxon Chemical Co. is expanding its metallocene catalyst technology for making polyethylene resins to include those made in loop-slurry-process, high-density PE units.

Indeed, by 1998 the company, based in Houston, TX, USA, plans to convert 114,000 tons of slurry capacity in the USA to make "plastomers", elastomeric, metallocene-catalysed, linear low-density PEs of 0.880 to 0.910 g/cm^3 density.

Among their features, plastomers offer cost-performance benefits in speciality films (e.g. breathable produce and freezer bags), in medical moulding, PP modification and other applications.

Exxon is not the only resin producer, or even the first, to adapt metallocene catalysts for slurry-process units: it has also been done by BASF, Ludwigshafen, Germany, Phillips 66, Bartlesville, OK, USA, and Borealis, Lyngby, Denmark. Exxon's step, however, strengthens its position in licensing metallocene PE technology.

In a separate move, Exxon is issuing a licence to Mitsubishi Chemical, Tokyo, Japan, to retrofit metallocene technology to an autoclave high-pressure unit in Japan. Mitsubishi is to supply plastomer grades to Pacific Rim markets by late 1997.

Exxon officials say they expect Mitsubishi to convert a 45,000 ton/year line in Okayama, Japan, to metallocenes by late 1997. Exxon is to provide technical and design assistance, and supply catalyst components.

Europe, too, is to have a plastomer supply source by early 1997. Exxon and DSM, Sittard, Netherlands, have a joint venture with plans to convert a 114,000-ton DSM solution-process unit to plastomer production.

The chief beneficiaries of Exxon's moves are 200 global processors (most in the USA) using or testing the company's plastomers in fast-growing niches. Exxon is producing plastomers in a 23,000 ton/year high-pressure unit in Baton Rouge, which is approaching its supply limit.

Implications of Exxon's latest moves are broad. The slurry process, a mainstream PE technology, is used to operate about a fourth of global PE capacity. Until recently, the process had been restricted to making conventional HDPE. Metallocene technology, however, allows slurry units to make HDPE, LLDPE and plastomers. (Source: *Modern Plastics International*, July 1996)

Metallocene-based PE is ready for rotomoulders

Borealis, Lyngby, Denmark, has started marketing new grades of Borecene metallocene polyethylene for rotomoulding after reaching a "freedom to operate" agreement with Exxon Chemical, Brussels, Belgium. Exxon holds broad patents on a number of metallocene or single-site catalysts. The company expects to make 40,000 tons/year of mPE. Metallocene catalyst is presently used only at the company's Norwegian loop slurry plant. But the company also expects them to be used in the company's bimodal, combined slurry/gas-phase reactors to produce HMW-HDPE resin. (Source: *Modern Plastics International*, February 1997)

Metallocene catalysts unit launches Univation joint venture

The world's largest facility for making metallocene catalysts for polyethylene (PE) production has been completed at Exxon Chemical's Mont Belvieu, TX site. The plant will produce enough catalyst to make 1.4 tons/year of PE. Plans are already on the drawing board for a second unit.

The facility was revealed at the launch of Univation Technologies, a PE technology development and licensing joint venture between Union Carbide and Exxon Chemical. The mission of Univation Technologies is to invent, develop and license PE technologies. Also, to develop, manufacture and sell metallocene catalysts.

Univation will offer Carbide's *Unipol* PE process, Exxon's *Exxpol* metallocene technology as well as Ziegler-Natta and chrome catalysts, and supercondensed mode technology for expanding reactor capacity. In addition to new plants, appropriate parts of the technology package will be offered for retrofitting existing *Unipol* and gas-phase plants and slurry PE plants.

Univation will include both Union Carbide's and Exxon Chemical's largest research efforts.

Univation will have access to 14 gas-phase and slurry process pilot plants, a 50,000 ton/year gas-phase reactor, a 20,000 ton/year slurry development line as well as commercial *Unipol* and slurry reactors. Capability for producing a low-pressure PE to replace high pressure LLDPE materials has been demonstrated in pilot plants trials. (Source: *European Chemical News*, 21-27 April 1997)

Montell and Dow move on metallocenes in polypropylene

Montell is negotiating to acquire rights to use Dow Chemical's INSITE metallocene catalysts in its Spheripol polypropylene (PP) process. If completed, the deal—an outgrowth of Dow and Montell's previously announced PP link—could dramatically speed penetration of metallocenes technology into the commodity PP market.

Montell aims to use INSITE technology in its Spheripol plant, but discussions are not complete. Montell Technology Co. licenses Spheripol and the Spherilene gas-phase polyethylene process.

Montell is the largest PP producer and Spheripol the leading PP technology, representing 35-45 per cent of installed worldwide PP capacity; technologies from Union Carbide and BASF—the closest competitors—represent about 10 per cent each. When Dow and Montell confirmed their PP deal—whereby Dow licenses Spheripol and the two companies swap PP—they said they would together evaluate the use of metallocenes in Spheripol; however, they did not detail the form that cooperation would take. Dow stressed that it would have rights to apply its metallocenes technology to any new Spheripol PP units it built.

However, there is a technical hurdle to using metallocenes in Spheripol. The heart of Spheripol is a spherical catalyst, a shape not yet used with INSITE.

Montell is not negotiating to link its Spherilene polyethylene (PE) process with Dow's Insite; Dow recently announced a deal linking INSITE with BP Chemicals' Innovene gas-phase PE process. Montell is instead working on its own technology, which mixes Ziegler-Natta and metallocenes catalysts to use with Spherilene. In June, the company began testing the technology in a 3,500 mt/year pilot unit at Ferrara, Italy, producing new grades of linear low-density PE and bimodal high-density PE.

The technology mixes the superior processability of Ziegler-Natta systems with the superior selectivity of metallocenes. But it is unclear whether Montell has a patent position strong enough to commercialize the technology without agreements with other metallocene players.

Spherilene, which was commercialized in 1994, is new to PE licensing and seriously trails the market-leading technologies of Union Carbide and BP Chemicals. Montell has sold three Spheriline licences in the past year, however, accounting for 40 per cent of new gas-phase licenses in the period, the company says. (Source: *Chemical Week*)

INSITE Technology

Since its introduction in December 1992, INSITE Technology, the Dow Chemical Company's patented constrained geometry catalyst technology has helped to revolutionize the global polyolefins and elastomers market-place.

INSITE technology creates value growth through broad and accelerated commercialization of new products, new business models and ventures. Product and material priorities include the development of new families of polymers, including: AFFINITY polyolefin plastomers (POPs) and ENGAGE polyolefin elastomers (POEs), new polyethylene resins enhanced via INSITE technology; and the development of other new novel polymers.

Dow has already been granted more than 50 US patents, resulting from its work with INSITE technology, including catalyst, process, polymer and end-use application patents. Dow has also been granted two European Patents (EPs) and more than 35 patent applications have reached the EP publication stage.

INSITE technology is based on a constrained geometry catalyst family that is chemically different from other metallocene-type catalysts. The INSITE catalyst is formally known as a "constrained geometry" catalyst because of its molecular geometry. This special geometry, which forces greater exposure of the active metal site, has many advantages, not least of which is the ability to make easier processing polymers with improved mechanical properties by incorporating long chain branching into the polymer structure.

INSITE technology was invented through Dow's efforts to develop high-performance catalysts for polyolefins manufacturing. Conventional linear low-density polyethylenes, for example, are produced via Ziegler-Natta catalysts, which feature multiple active sites. Multiple active sites create polymers with varying molecular structures, resulting in variable distribution of the comonomer between polymer chains, depending on the comonomer.

The INSITE catalyst, by comparison, has only one active site. A single site tends to polymerize in a more uniform fashion, so that every molecule is similar—polymer chains are more consistent in length, and have more consistent incorporation of comonomer into the polymer—which results in a narrow molecular weight and comonomer distribution. This uniformity leads to exceptional, very predictable physical and mechanical polymer properties. INSITE technology enables production of polymers with long chain branching, which makes them easier to process than other ethylene-alpha-olefin copolymers having a narrow molecular weight distribution, but no long chain branching. Additionally, copolymers produced via INSITE technology have the positive attributes of superior optics, low heat seal initiation temperature, low extractables and high dart impact strength.

INSITE technology is based on constrained geometry catalysis, which refers to the bond angle that opens up the catalyst site, enabling the incorporation of long monomer chains.

INSITE constrained geometry catalyst technology is unique for three reasons:

1. It creates new compositions of matter;
2. It breaks traditional polymer-structure property relation rules; and
3. It allows enhanced speed to markets, cutting conventional development and commercialization cycles dramatically.

Because of its flexibility, INSITE technology can incorporate a variety of comonomers. Precise, predictable molecular architecture is a distinguishing feature of INSITE constrained geometry catalyst technology.

In general, single site catalyst technology is known to produce random olefin copolymers with very narrow molecular weight distribution (MWD) and comonomer, or short chain branching distribution (SCBD) which together improve physical properties.

One of the unique aspects of constrained geometry catalysis, Dow's proprietary single site catalyst technology, is its ability to create long chain branches (LCB) on narrow MWD polymers. Together, the narrow MWD and LCB have been demonstrated to deliver excellent processability and superior mechanical performance, eliminating the sacrifice of one for the other, as is often required by conventional technologies.

Dow is actively pursuing the use of INSITE technology to produce resins for a broad spectrum of applications. Products such as polyethylene resins enhanced via INSITE technology are being designed and developed to meet the needs of today's demanding polyethylene applications. Industrial and consumer cast and blown films; food and speciality packaging films; and injection and rotomoulded articles, as well as extruded sheet and profiles are a few of the potential applications for these resins.

Another new type of resin made possible by INSITE technology is Ethylene-Styrene Interpolymers (ESIs) made through copolymerization of ethylene and styrene, which yields materials with unique properties that are not observed in either polyethylene or polystyrene homopolymers. ESIs offer customers a rigid plastic that can be readily formed and reformed. Applications for these polymers include, but are not limited to, packaging, general durables, wire and cable, toys, automotive, general elastomers, gaskets and profiles.

INSITE technology is also bringing value to joint ventures and global supply agreements. In August, BP Chemicals Ltd. and The Dow Chemical Company announced a joint development agreement to develop and make available for licensing a combination of BP's Innovene 1 gas-phase PE process and INSITE catalyst technology developed by Dow. The two companies began joint development of INSITE constrained geometry catalyst in the Innovene process in 1995, and have successfully demonstrated the capability to produce high-performance polymers from a gas-phase process with constrained geometry catalysts. The technology has the potential to produce products with superior processability, impact strength, heat seal and optical properties made possible by INSITE catalyst, coupled with the economic benefits of Innovene technology.

Dow's advanced constrained geometry catalyst technology also helped put into motion the first phase of a global strategy to become a leading supplier of polypropylene (PP). Dow's PP market entry plan consists of a commitment to metallocene development for PP products, global supply agreements with Montell Polyolefins, licensing of SPHERIPOL process technology for PP manufacturing, and new plant construction. With the potential to impact PP as significantly as it has PE, Dow's catalyst technology continues to contribute major performance and processing benefits that will fuel new uses, new demands and above-average growth rates. (Source: *http://www.dow.com/plastics/news/insite.html*, Dow Plastics Newscenter, 12 December 1997)

Dow delivers long-awaited metallocene LLDPE

Dow Chemical has announced the commercialization of linear low-density polyethylene (LLDPE) resins made using its INSITE single-site catalyst technology. The company says it expects to invest $500 million by the year 2000 for 1.21 billion tons/year of solution-phase capacity at five sites.

Dow says it started up a 200,000 tons/year unit at Plaquemine, LA, in December 1996 to make the LLDPE, converting an existing Dowlex LLDPE unit to the new catalyst technology. A 210,000 tons/year INSITE plant is scheduled to come onstream at the BSL complex in Schkopau, Germany, in the first quarter of 1998. It was originally slated to make Dowlex. Dow plans to build additional capacity for INSITE LLDPE in Canada, Argentina and Thailand over the next three years.

The octene-based LLDPE products mark a major effort by Dow to apply its Insite technology—which uses catalysts closely related to metallocenes—to commodity PE production. Dow previously introduced speciality polyolefins, including PE-based plastomers, based on Insite. But tapping into large-volume PE markets has long been a goal of metallocene developers.

The new Dow products, which will be trade named Elite, will be sold as high-performance LLDPE. Dow will initially market the resins between its Dowlex LLDPE and the company's line of speciality polyolefins.

Dow is introducing four elite grades, including those for use in products such as shopping bags and food packaging. (Source: *Chemical Week*, 5 March 1997)

Triunfo selects BP technology

Brazil's Petroquimica Triunfo has signed a letter of intent to license BP Chemicals' Innovene gas-phase technology to manufacture 130,000 tons/year of high-density polyethylene (PE) and linear low-density PE at Porto Alegre. The project has been planned for years but has been held up in part by judicial roadblocks to the privatization of Petroquimica Triunfo.

The letter of intent is for BP's Innovene high-productivity license, including high-strength hexene copolymer and an option on next-generation technologies, including metallocene catalysts. The option would include the Innovene process and Dow's metallocene catalysts. BP and Dow are forming a venture to license the technology; once the BP-Dow technology package is commercialized, Triunfo will have the right to purchase it. (Source: *Chemical Week*, 5 March 1997)

Metallocene LLDPEs

Most extruders designed for conventional linear low-density polyethylene (LLDPE) can process Exceed metallocene linear lows (mLLDPE) without difficulty; torque, head pressure and motor load limitations generally do not limit film productivity. However, it is important to understand the differences arising from the different rheology of Exceed mLLDPE from Exxon Chemical.

Exceed mLLDPE has a narrower molecular weight distribution, and it thus exhibits lower shear sensitivity. All other things being equal, they are more viscous at typical extrusion shear rates than conventional LLDPE resins.

If Exceed LLDPE and Ziegler-Natta (Z-N) LLDPE are both extruded with the same LLDPE screw using the same barrel profile, Exceed mLLDPE will extrude at higher melt temperatures. The higher melt temperature may limit output (1b/hour) on cooling-limited lines (but it may be possible to keep line speeds constant—thereby making a thinner film having the same performance—because of the better properties offered by Exceed mLLDPE).

Barrel cooling can be used to reduce mLLDPE melt temperatures, but it may be more desirable to optimize the extruder screw for the rheology of Exceed mLLDPE.

Approaches to this problem will be discussed, but it is first worthwhile to review the basic functions of a simple extruder screw.

A simple screw has at least three zones, each with a specific function. The first zone is the feed section, where the solid polymer is introduced to the screw, compressed and compacted. The second zone is the transition section, where the compacted polymer begins to melt. In the transition section, the frictional forces on the compacted polymer bed steadily increase as the screw depth decreases. The associated mechanical energy is dissipated as heat, which raises the temperature of the polymer and ultimately causes it to melt. The amount of mechanical energy applied to the resin, and hence the melt temperature, depends in part on the screw design.

The third functional zone of a screw is the metering section, where homogenization and pumping of the melt take place. It is important to keep in mind that the objective of the screw is to deliver a homogeneous melt at a constant target melt temperature and constant flow rate.

As solid polymer melts, it flows across the barrier flight clearance and into the melt channel. Shear is imparted to the melt, and the resulting mechanical energy is dissipated as heat. The narrower the clearance, the higher the shear rate over the barrier clearance, and the greater the viscous heating. Viscous heat generation will be very dependent upon the barrier clearance, as well as upon the power law index of the melt.

Mixing elements are another important source of viscuos heating. Most are shear mixers that rely on the application of shear to the polymer to homogenize the melt. These mixing elements also have barrier clearances across which all of the polymer melt must flow. Again, the narrower the clearance, the higher the shear rate across the clearance and the greater the amount of viscous heat generation. Widening the barrier clearance in the mixer, like widening the barrier clearance in the screw, will tend to impart less energy (and lower mixing) to the polymer melt.

The screw designer may consider, therefore, slightly larger barrier clearances in the dual-channel screw for processing Exeed mLLDPE, and it may also be beneficial to increase the clearance in the mixing section, provided that these changes can be made without an unacceptable loss of melt homogeneity.

Most dies designed for Z-N LLDPE work well with Exceed mLLDPE. The typical die for blown film is a bottom fed spiral mandrel die. As is the case for Z-N LLDPE, wider spiral clearances will beneficially reduce die pressure. Thus a "low pressure" spiral design is desired.

Exeed mLLDPE, like Z-N LLDPE, has a tendency to melt fracture at the melt temperatures and shear rates used in blown film extrusion. They are therefore best extruded out of moderately wide die gaps (60-90 mils) with the use of a polymer processing aid (PPA). Exceed mLLDPE for most blown film applications contains PPA as supplied.

Higher die pressures are undesirable because they can lead to lower outputs and higher melt temperatures. Net output is the sum of two terms: drag flow and pressure flow. Drag flow occurs as a result of the rotation of the screw root with respect to the barrel wall, and it is analogous to the flow induced in a fluid contained between two parallel moving plates. Pressure flow directly opposes drag flow, is negative in sign, and becomes larger as the pressure gradient in the metering zone increases. Constriction in the die will cause higher head pressures and will therefore increase the pressure flow term (i.e. make it more negative). Finer screen packs will do the same.

Thus, at a constant screw rpm, the net output drops as the die becomes more restrictive, and in order to obtain the same output, the screw speed must be increased. The increased screw speed results in more mechanical energy being applied to the melt and thus, a higher melt temperature.

Exceed mLLDPE crystallizes at a temperature of about 5-6° C below the crystallization temperature of Z-N LLDPE. As has also been noted, Exceed mLLDPE will tend, all other things being equal, to run hotter than Z-N LLDPE. Cooling efficiency is therefore very important, and air rings should be of the dual-orifice type. Chilled air is recommended.

Extra bubble stability enhancement, such as extended cones, protective shrouds, irises, and secondary air rings can be beneficial (irises are often used in combination with protective shrouds). Naturally, the addition of an IBC unit would also improve cooling efficiency.

Dual orifice air rings supply two flows of air. The lower air flow produces a Venturi effect which tends to hold the bubble in a stable, fixed position. The upper air flow provides the main cooling effect. With the stabilizing effect provided by the Venturi, more cooling air can be applied to the bubble. While this is a significant improvement, the cooling air still diffuses rather rapidly away from the bubble.

The addition of a bubble stability enhancement device prevents diffusion of the cooling air away from the bubble until the cooling air has contacted a much larger portion of the bubble surface. In addition, the turbulence observed in the single orifice or dual orifice cases is reduced, thereby permitting higher air flows to be applied to the bubble surface. The net result is an improved cooling capacity which can be very beneficial to running metallocene resins.

To summarize the processing considerations for Exceed mLLDPE: most existing LLDPE equipment can process Exceed mLLDPE well, but compared to Z-N LLDPE, mLLDPE will extrude hotter. On cooling-limited equipment, these effects may reduce crates 5-10 per cent. Rates may be improved by implementing the following:

- Screws having larger barrier clearances (provided melt homogeneity is not unacceptably sacrificed);
- Lower pressure dies and coarser screen packs;
- Air rings having enhanced bubble stabilizing features such as irises, extended cones or protective shrouds.

Table 1

How mLLDPE properties impact processing

Polymer property	**Interpretation**	**Implication**	**Process impact**
Narrow MWD	Fewer low MW lubricants	Higher process pressures	Higher melt temperature
		Higher torque	Change motor size of RPM
	Fewer low MW extractables	Low film blocking	Easier winding/unwinding
	Fewer high MW stiffeners	Lower melt strength	Decreased bubble stability
			Easier drawdown
		Higher clarity	
Less chain branching	Fewer entanglements	Faster melt relaxation	Less draw resonance
			Easier drawdown
Lower density		Soft, tacky	Decreased specific behaviour rate in grooved-feed machines
			Increased specific rate in smooth-bore machines
			Increased collapser friction
	More elastic behaviour	Sensitive to tension	Harder to wind

Source: William Hellmuth, senior product manager Battenfeld Gloucester Engineering. This table is an effort to simplify the correlation between resin properties and processing. (Source: *Plastics World*, July 1996)

First MPPs go commercial in Europe

Hoechst AG and BASF AG in Germany are commercializing their first isotactic homopolymer metallocene polypropylene (MPPs). Copolymers are coming next.

For now, the new MPP grades are available only in Europe, but both companies could potentially license them here, as they are made in commercial polymerization processes.

Hoechst announced two commercial-scale trial runs of MPP, made in a 400-million-lb/year Spheripol plant near Cologne, Germany, licensed from Technopol/Montedison in Italy. BASF used its own Novolen gas-phase process, which is also commercially licensed.

Propylene monomer, with its right- and left- handedness, can make for more complex chain possibilities when assembled with single-site catalyst precision, than polyethylene. This has made MPP slower to develop than MPE. Single-site metallocene catalyst makes resins with a high degree of stereospecificity or statistically induced chain irregularities. That means a molecular mistake is inserted at regular intervals along the polymer chain.

Metallocene MPPs show narrower molecular weight and comonomer distribution, with a wider range of possible comonomers and more even comononer distribution than conventional PP. They can also access very high molecular weights of isotactic PP, compared to conventional Ziegler-Natta catalyst PP.

New MPPs show outstanding properties of toughness and stiffness, improved modulus, hardness and transparency and extremely low exractables.

Properties of MPP that are catalyst-tailored include molecular weight distribution, degree of isotacticity and consequently melting point.

BASF's MPP also has a unique microstructure that leads to a lower melting point of 293° F, which translates into a narrow relaxation time spectra—without the extremely long relaxation times from any ultra-high molecular weight portion in the polymer—allowing faster stress relaxation on plastic deformation. The lower melting point indicates a shorter long period in the crystal lattice, leading to a higher number of tie-molecules between different crystallites. Both are advantages in biaxially oriented polypropylene film (BOPP) compared to conventional PP.

Thinner films with improved tensile strength and superior optical properties can be produced at significantly reduced processing temperatures.

Hoechst uses metallocenes or a mixture of metallocenes supported on inert carriers, in a bulk reactor and said its process is becoming competitive with conventional catalysts. BASF uses a proprietary metallocene which is retrofittable for use in existing Novolen gas-phase reactors.

Hoechst shares catalyst technology with Exxon Chemical Corp., Houston, which in September 1995 commercialized the first isotactic MPP—tow grades for spun fibre. Other resin companies that have developed MPP include Fina Oil & Chemical Co., Dallas, and Mitsui Toatsu Ltd. in Japan, both of which have also made commercial-scale trials of syndiotactic PP. (Source: *Plastics World*, May 1996)

How metallocene PPs compare to conventional

	BASF	**Hoechst**	**Conventional**
	Homopolymer MPP Extrusion	Homopolymer XAW11A SAD Injection	Homopolymer PP Extrusion
Melt flow rate, g/10 min.	8	60	2.5
Gauge, microns	12		18
Melt temperature, °F	284-302	302	320-338
Tens. str., N/mm^2 MD	134		120
TD	362		260
Elong. at break, per cent MD	210		200-240
TD	37		40-50
Tensile modulus, M/mm^2		1,500	
MD	1,700		2,000
TD	3,110		2,800
Unnotched impact, mJ/mm^2		6.5	
Haze, per cent	0.1		2.5
Transparency, per cent		80	
Gloss	116		85-90

Source: Metallocene 196

Table provides clues as to property edges mPPs hold

(Source: *Plastics World*, May 1996)

Metallocene catalysts—research and systematic development at Hoechst

In the area of organic chemistry, a generational change is under way. A new family of catalysts—known as metallocenes—will replace the customary Ziegler-Natta systems in wide sectors of polymer manufacture over the next few years. This development marks a quantum leap in polymer synthesis because, by using metallocenes with a sandwich-like steric configuration, it is now possible for the first time to produce plastics with a property profile that can be precisely controlled within wide limits.

Until recently, this precise balancing of different properties such as heat resistance, hardness, impact strength and transparency has not been possible. The reason for this is that conventional Ziegler-Natta catalysts are generally solids on whose surface a relatively heterogeneous process of catalysis takes place. This gives rise to a polymer of correspondingly heterogeneous composition. Since the catalyst itself is insoluble, its active sites are virtually impossible to detect analytically. It cannot therefore be systematically improved on a rational basis.

In contrast to this, a metallocene catalyst has a single active site. This key point in polymer synthesis can be studied in close detail because of the good solubility of the complex. For this reason, the individual steps by which the catalyst links up the monomer units into a chain are known in principle. Building on this knowledge, it is possible to modify metallocenes—unlike Ziegler-Natta systems—so that the structure and properties of the plastic produced can be far better controlled than previously.

Back in 1985, Hoechst embarked on an extensive research project to study the promising new family of the metallocenes in detail. In that same year, university professors Hans H. Brintzinger (Konstanz) and Walter Kaminsky (Hamburg) showed in a sensational scientific publication that certain zirconium-containing metallocene types offered promising industrial potential. Using these catalysts, researchers had succeeded in producing a certain type of polypropylene (PP)—known as isotactic polypropylene (IPP)—with high yield and purity.

The steric configuration of this plastic is such that the methyl group of the polypropylene molecule—looking along the polymer chain—branches unidirectionally on one side only. This ordered structure (chemists speak of "stereoregularity") in itself gives the plastic improved properties in many respects.

But by using metallocenes, it was possible for the first time actually to control the degree of this ordering and hence to "engineer" the properties of the polymer so produced. For example, the melting point of an iPP based on metallocene catalysis can be varied between 130 and 160° C according to the application.

Because of their traditionally strong position in the field of organic synthesis, Hoechst research chemists succeeded in developing a number of elegant synthesis methods for the extremely complex preparation of metallocenes in a relatively short time. In the field of metallocenes of the bis-(indyl)-zirconium complex type, which are of particular industrial importance to Hoechst, this work marks the limit of what is technically feasible in the world today.

Between 1987 and 1995, more than 100 new zirconocenes were synthesized and thoroughly tested under this project. The most active representatives of this type are far superior to conventional catalysts. From 100 g of metallocene, some 100,000 kg of plastic can be produced. Conventional systems achieve at most only fractions of this performance.

On the basis of this extensive experimental experience, the Scientific Computing working group in the central research department supported the systematic development of highly active metallocenes with powerful simulation and modelling programs. It is now possible to represent the individual steps of the catalytic process at molecular level. In this way, systematic optimization of metallocene catalysts can be more effectively carried out.

Metallocene activities at Hoechst over the next few years will focus among other targets on the industrial manufacture of isotactic polypropylene (iPP). The properties of this plastic are superior to those of conventionally catalysed PP grades in some respects (higher stiffness, adjustable melting point, increased transparency, low extractables) and thus open up new and more sophisticated applications for this long-established material. Polypropylene will capture applications which until very recently appeared to be the preserve of engineering plastics. The support system for the metallocenes used to produce this plastic has been developed to production readiness as part of R&D cooperation between Hoechst and Exxon continuing since mid-1994.

An important advantage of the new metallocenes is that no fundamentally new production processes are required for their use in the manufacture of plastics. They are suitable for existing industrial production plants. All that needs to be done is to replace conventional catalysts with far more efficient metallocene catalysts specially adapted to the particular process (drop-in technology).

Hoechst is working intensively at present to introduce the new metallocene catalysts into its own production plants. As part of this programme, an initial production trial is planned. Commercial production of metallocene-based iPP is expected within the next two years. With its extensive experience and strong patent position, Hoechst would also like to manufacture metallocene catalysts on a commercial scale in future and make them accessible to other interested parties at a later stage for drop-in technology.

Developments in the field of metallocenes and know-how related to their use will make a significant impact on the polyolefin industry over the next few years. The new technology will give additional growth impetus to this sector—particularly to the strongly growing PP market. In only 10 to 15 years, half of the world's polyolefin capacity could be based on metallocene catalysts.

For more information, contact: Hoechst Aktiengesellschaft, Corporate Communications, 65926 Frankfurt/Main, Germany. Fax: +49 69 305 16357 (Hartmut Vennen); E-mail: vennen@msmzoea.hoechst.hoechst-ag.d400.de; Web site: http://www.hoechst.com.

New applications for BASF's metallocene PP Basic polyolefin patent safeguards rights

BASF AG unveiled the first target applications for the company's new metallocene homopolypropylenes at the "Metallocenes '96" Conference held in Düsseldorf. Thanks to the combination of narrow molecular weight distribution and a unique microstructure, giving lower melting polymers with reduced lamellar thickness of the crystalline portion, the materials provide better performance when stretched in the partly molten state. Thus, they are superior to conventional polypropylene for high-speed fibre spinning. In particular, finer fibres with higher tensile strength can be spun at the high spinning rates typical of polyamide. Also in biaxially oriented PP (BOPP) film production, thinner films with improved tensile strength and superior optical properties can be produced at significantly reduced processing temperatures. The advantages of the new materials have been confirmed by the first positive feedback from customer trials.

The new polymers are produced by BASF's Novolen® gas-phase process, using a unique proprietary metallocene catalyst. Metallocene homo-polypropylene, random and impact copolymers have already been continuously produced successfully using this catalyst system.

During the last few years BASF has devoted significant efforts to the development of a "drop-in" metallocene technology, which is retrofittable in its versatile Novolen process. The new materials from this technology will complement the existing Novolen PP product range based on BASF's PTK 4W high yield catalyst system.

BASF is worldwide the only company with proprietary PP production technology, a proprietary high-yield catalyst system and proprietary metallocene technology.

BASF's new metallocene technology, which will be licensed together with the Novolen gas-phase PP technology, is protected by a broad range of more than 90 patents and patent applications, embracing catalysts, products and applications, in the PE and PP field. BASF's portfolio includes the composition-of-matter patent for its metallocene PP catalyst (US 5,296,434) and the product patent for the polymer obtained with this catalyst for which the US Patent Office has recently issued the notice of allowance. Moreover, BASF also holds the first patent covering the use of methylaluminoxane-activated, unsubstituted and substituted zirconocenes as polymerization catalysts for ethylene and propylene (US 4,404,344). BASF intends to make active use of its rights from this early metallocene patent. Web site: http://www.basf.de. (Source: *BASF Aktiengesellschaft*, recent press release, 3 July 1996)

Harrel announces tubing lines optimized for metallocene polymers

Harrel Incorporated is now offering a family of turn-key plastic extrusion lines designed especially for use with the new metallocene-catalysed polymers such as Dow/Dupont Engage®. These polymers are the first ones on the market which show real promise for replacing PVC (polyvinyl chloride) in tubing extrusion.

The Environmental Protection Agencies in a number of states and communities in the USA have expressed a desire to do away with PVC wherever possible. Counterpart regulatory bodies in other countries—Germany and Scandinavia in particular—have done likewise. Up until now, however, there has been no cost-effective, viable alternative. Dow/Dupont's Engage is not only cost- competitive with PVC but also has similar flexibility and other properties. The metallocenes also have the enormous advantage to the processor that they degrade less readily than PVC and are therefore much easier to process.

There are, however, special characteristics of the metallocene materials, and, while they can be processed on regular extrusion equipment, the extrusion performance can be greatly improved by modifying both extruders and downstream equipment to handle them more readily. These turnkey extrusion lines are optimized from the hopper to the final conveyor to handle metallocenes. Appropriate changes have been made in the screws, the die, and most particularly, in the downstream equipment.

At the same time, all of the automation and the closed loop control of final tubing dimensions and characteristics have been retained. The patented Harrel TUBETROL® process controls both the outside diameter and the inside diameter of both the large and small sections of bump tubing, or of all three sections of double bump tubing.

And with suitable modifications to the new Alternate Polymer Tubetrol system of Harrel, metallocene resins can be used as one of the components in a tube whose polymer composition is changed as a function of length along the tube.

Harrel tubing lines range from 3/4 inch and 1 inch, making microbore tubing for medical applications, all the way up to 2-1/2 inch and 3-1/2 inch lines making 2 inch diameter, thin wall tubing, for cosmetic or food squeeze tubes.

For more information, contact Harrel Inc., 16 Fitch St., Norwalk CT 06855, USA. Fax: +203 866 1483; E-mail: info@harrel.com. Website: http://www.harrel.com

The future?

Shell Chemical's introduction recently of its line of Carilon aliphatic polyketones marks the debut of one of the few novel polymers to be commercialized in recent years. The Shell polymers may be only the tip of the iceberg, however, as a new generation of late transition-metal catalysts redefines the possibilities of olefin polymerizations.

Like their metallocene cousins, they are single-site, homogeneous catalysts that allow the precise—and extremely predictable—tailoring of polymer chains; however, the nickel (Ni) and palladium (Pd)-based catalysts perform a variety of tricks not easily done with conventional catalysts or metallocenes, including synthesizing highly branched polyethylene (PE) and copolymerizing olefins with carbon monoxide (CO).

They represent the next wave [after metallocenes] in polymer catalysts, according to BFGoodrich's chemical sciences department (Brecksville, OH). The catalysts' ability to polymerize olefins containing functional groups, such as esters and acrylates opens up a whole new area of catalysis.

While the full commercial impact of the catalysts is still probably years away, a handful of leading polymer producers, including DuPont, Goodrich, BP Chemicals and Shell Chemical, are betting heavily that the technology will lead to a range of lucrative new polymers. Shell estimates that its Carilon line of polyketones could eventually grab a $1 billion/year piece of the engineering plastics business. Goodrich is pinning its hopes on norbornene-based cyclic-olefin polymers that have a range of promising properties, including heat resistance.

No one has higher ambitions for the catalysts than DuPont, however. The company, which has lagged behind industry leaders in developing metallocenes and other new polyolefin catalysts, has funded development of late transition-metal catalysts at the University of North Carolina (UNC, Chapel Hill) and announced in early 1996 that it had filed a 500-page patent application—the largest in its history—covering the technology. The catalysts could allow the synthesis of novel polyolefins in every polymer-based business and lead to lower-cost and more flexible synthesis processes.

Polymer makers are intrigued because the late transition-metal catalysts appear to overcome many of the limitations of other polyolefins catalysts, including metallocenes. Metallocenes and conventional polyolefin catalysts are, for one thing, notoriously intolerant of elements other than carbon and hydrogen. As a result, they have difficulty polymerizing olefins containing various functional groups or copolymerizing olefins with monomers such as CO.

However, chemists at UNC, Shell and a handful of other laboratories have overcome the problem by moving across the periodic table, using late transition metals, such as Ni and Pd, rather than the early transition metals, such as zirconium and titanium, typically found in metallocenes. The resulting Ni- and Pd-based catalysts are active in polymerizing a wide range of monomers. Further, the Ni-based versions of the catalysts have shown high activity in polymerizing ethylene to form highly branched, amorphous PE.

The most commercially advanced polymers based on the technology are Shell's Carilon polyketones, which are made using a Pd-based catalyst. Shell started up its 40-million lb/year production unit in Carrington, UK, in early October 1996 and is selling the polyketones in Europe and the USA.

Key to the technology and the unique properties of the polymers is that the single-site Pd catalyst polymerizes CO and olefins in a perfectly alternating structure. The results are semicrystalline materials with engineering plastic properties. In addition, the single-site nature of the catalyst means the molecular weight distribution and molecular chain distribution can be very well defined.

Other research groups have developed related catalysts but have focused on different polymer materials. Led by Maurice Brookhart, UNC chemists have also developed Ni- and Pd-based catalysts; but the UNC group is using the catalysts to make novel ethylene and propylene homopolymers as well as ethylene copolymerized with olefins containing functional groups.

Most advanced, and one of the most exciting areas of development, is an Ni-based catalyst that is capable of polymerizing ethylene into highly branched PE. PE made using metallocenes or conventional Ziegler catalysts is linear, with little branching and a relatively high melting point. To make branched PE using such catalysts typically requires a comonomer, such as hexene or octene.

In contrast, the Ni catalyst can make a range of ethylene homopolymers, ranging from linear, semicrystalline polymers to highly branched, amorphous PE. The payoff in controlling the branching could be the development of an elastomeric PE that does not require a comonomer.

DuPont shares the patents covering the technology with UNC and holds the exclusive worldwide rights to the catalysts.

Meanwhile, Goodrich researchers have developed Ni and Pd catalysts to polymerize norbornenes. The catalysts are capable of making a whole family of norbornenes [polymers], with almost any functional group you can imagine.

Transparent norbornene hompolymers have been made with a glass transition temperature of 390° C—a property that could make the polymers useful as an engineering plastic—and has controlled the molecular weight of the polymers from a few hundred to several million. In addition, techniques to tag various olefin groups, including ethylene and isboutylene, onto the end of the polymer chains have been found. The polymerization of norbornenes containing functional groups, such as carboxylic acid, esters and alcohols is also being developed.

Next-generation catalysts?*

Groups	Technology	Status
Shell Chemical	Pd-based catalysts; carbon monoxide-olefins copolymers	1996[1]
BP Chemicals	Pd-based catalysts; carbon monoxide-olefins copolymers	Pilot plant[2]
DuPont—University of North Carolina	Ni and Pd-based catalysts; polyolefins with novel branching; polymerization of olefins with polar comonomers	NA
BFGoodrich	Ni- and Pd-based catalysts; cyclic-olefins polymers based on norbornenes	Two to three years from commercialization
W.R. Grace—California Institute of Technology	NA	Research project

Source: Company reports.

* Includes companies reporting work on late transition-metal catalysts used for olefins polymerization.

[1] Carilon introduced in USA in October.

[2] Pilot-scale units running at Grangemouth, UK.

NA: Not available.

(Source: *Chemical Week*, 20 November 1996)

H. INFORMATION RESOURCES

Traders hit the superhighway

Polymer trading has entered the Internet era with the 13 January launch of a web site by Amsterdam-based company, First Polymer Market. The site is privately financed, and is intended to provide global players with an interactive meeting and trading place.

A $300 annual membership fee allows access to the site and the ability to make international offers and inquiries. First Polymer Market will soon expand its services into associated areas, such as transportation, customs clearance, warehousing and insurance, to provide a full service package for its users.

Although many producers are wary of such a move, one major West European producer said: "It is no bad thing. You cannot hold back progress. Already traders fax product offers and prices throughout the world. This move is inevitable." But, the implications are dramatic in terms of market transparency, with bids and offers likely to be available to a much wider audience.

The increased transparency was likely to lessen price volatility rather than increase it.

Several players feared that lack of control over data input into the system left it open to manipulation, citing the possibility of inputting false information. For instance, a player could move material between subsidiaries to set a price in the market.

Probably the most significant negative at this stage is the reluctance of many European producers to be involved in this highly visible marketplace. To overcome the traditional reticence of polymer producers, a system is in place to allow offers to be made anonymously through a mailbox facility.

The anonymity of the seller does not matter as much as transparency. They fear the fundamental market supply/demand situation will become crystal clear if all transactions are in the public domain through low-priced Internet access. (Source: *Chemical News*, 20-26 January 1997)

CIA's Sourcerer

Information about UK chemical products and suppliers is available on the Internet from the Chemical Industries Association (CIA) electronic product directory, known as Sourcerer.

Sourcerer offers visitors a "fast and cost-effective way" of obtaining accurate information about chemicals offered by UK manufacturers, claims the CIA.

The data on Sourcerer is drawn directly from the directory that the CIA also publishes about industrial products and suppliers.

The site, which was set up with financial help from the Department of Trade & Industry under the Export Challenge Initiative, contains information about 36,000 products from 3,500 companies.

"That makes it the only comprehensive source of chemical products for the UK on the World-Wide Web", the CIA claims. Sourcerer's URL is http://www.sourcerer.co.uk (Source: *Process Engineering*, February 1997)

UK Trade aims to be "virtual business centre" on Web

A Web site touted as "the world's first virtual business park, where companies can conduct electronic commerce on the Internet" has recently been launched.

UKTrade should put British exporters in touch with customers all over the world. The site is part of the Information Society Initiative Programme for Business.

At the heart of the site is a directory of British companies, which will go "live" in March, when the URL will also be announced. The directory will offer links to individual sites and enable customers to e-mail sales inquiries.

Computer company ICL is developing the directory and will be working with the Federation of the Electronics Industry and the Computing Service and Software Association to develop membership.

Contact: E-mail aldo_pelosi@compuserve.com (Source: *Process Engineering*, February 1997)

I. CONFERENCE NEWS

SPO Conference

Global compounding spotlights metallocenes

Not only is the global compounding business booming—it is taking on a new profile fueled by increasing use of metallocenes. What promises to be the biggest change the industry has ever seen is being revealed by compounders who are finally willing to talk about how much this new breed of resins can bring to the compounding table. That is the message delivered by speakers at the Specialty Polyolefins Conference (SPO '96), Houston, 25-27 September 1996.

Co-sponsored by *Plastics World* and sister publication *Plastics Formulating & Compounding*, SPO's compounding session was devoted exclusively to breakthoughs in metallocene compounding.

Perhaps not surprisingly, the bulk of this (disclosed) metallocene activity is coming from Asia and Latin America, where independent compounders without too many preconceptions or secrecy constraints appear to have taken massive advantage of the instant benefits that in many cases can be conferred by incorporating metallocenes into new compounds.

For example, in a paper by Daniel L. Davidson, president of DerriTech Consultants International, Asian technical innovation in using metallocene polyolefins (MPOs) is divulged in detail. Particularly in Taiwan and the Philippines, compounders have highly active programmes using MPOs as compounding modifiers.

One of the most interesting examples is from D&L Industries, an independent compounder based in Manila. According to Sonia Salvador, the compounder's technical manager, the flexible PVC crown liner compounds it had been supplying to beer and soft drinks bottlers were becoming unacceptable due to environmental concerns.

D&L turned to MPO to develop a grade with a unique combination of characteristics. Since MPO possesses all of the desired characteristics (FDA approval; sealing and gas barrier, sealing force; taste and odour), D&L prepared development samples of a blend of 10 per cent LDPE with MPO to slightly increase the melt index closer to the PVC grade.

D&L's product was the softest, but the customer wanted a compound that processed at a still lower temperature. They then prepared another sample based on higher concentrations of high melt index LDPE to lower the processing temperature and increase the melt flow.

Developments in cable

According to a paper by Robert J. Keefe, BICC Cables and Jim Hemphill, DuPont Dow Elastomers, use of metallocene resins in medium voltage filled insulation compounds has given engineers the ability to design polymer molecular architecture to optimize processing and end-use performance. The authors reported that a pelletizable metallocene-based compound can be designed with an optimum copolymer grade to give higher tensile and cold green strengths, as well as high flexibility.

Some single-site metallocene constrained geometry catalysts (CGCT) have a catalytic site for large comonomers, including vinyl terminated polymers. Insertion of vinyl terminated comonomers into the polymer chain facilitates long chain branching, thus enabling shear sensitivity closely resembling that of a wider molecular weight distribution Ziegler-Natta polymer.

The authors said that this results in ability to process CGCT polymers at comparable conditions to conventional resins, while at the same time minimizing melt fracture encountered with linear polymers, which do not have long-chain branching capabilities.

MPOs and additives

Along with metallocene modifiers and metallocene alloys and blends, a new generation of additives that takes fuller advantage of their potential is also emerging. A presentation by Joseph Radosta of Specialty Minerals Inc. described how a new ultrafine talc in combination with metallocene impact modifiers imparts higher heat resistance to polypropylene compounds.

Radosta said these new polypropylene compounds qualify for many new applications (such as under-hood components) that require greater resistance to deformation while under load at elevated temperatures.

Metallocenes can now be compounded with dramatic reductions in flame retardant additives levels to provide superior performance without sacrificing safety, reported Ronald L. Markezich of Occidental Chemical. Among the compounds tested were several using CFR in combination with magnesium hydroxide, antimony oxide, silica and zinc borate. Each formulation gave excellent flame retardance with only 25 per cent letdowns of CFR.

Complete papers are available from SPO Conference organizers Schotland Business Research, 16 Duncan Lane, Skillman NJ 08558. Tel.: (609) 466-9191, Fax: (609) 466-8833. (Source: *Plastics World*, December 1996)

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TECHNOLOGY AND INVESTMENT OPPORTUNITIES

SELECTED INVESTMENT/TECHNOLOGY REQUESTS

OLEORESIN PROCESSING

A successful producer of oleoresin, such as oleoresin paprika, oleoresin capsicum, oleoresin ginger and oleoresin turmeric has identified several production problems requiring alteration or replacement. Presently the company uses a hammer mill dry grinder, which can cause damage to certain raw materials. The company requires wet grinding equipment, utilizing cold imersion in the extraction solvent, which will eliminate product decomposition. An essential oil distiller is another important piece of equipment as the company intends to expand current production to include essential oils. Modifications are required to the existing continuous extractor to facilitate ease of extraction, thus increasing yield and production capacity. **Preferred Mode of Cooperation:** Equipment supply and R&D consortia.
For further information, contact: General Manager, Ethiopia Spice Extraction Factory, P.O.Box 5699, Addis Ababa, Ethiopia. Tel:+251 1 653300; Fax: +251 1 653633

ASSEMBLY PLANT FOR SMALL TRACTORS

A new project exists to assist small farmers to increase their productivity by providing them with mechanized tillage by way of tractors. The project itnends to set up a small-scale assembly plant to produce the tractors for sale to the farmers. Several mechanical workshops will need to be equipped to assemble and service the tractors. Spare parts will be needed in sufficient quantities to ensure the long-term usage of the equipment. Training is envisaged as a large part of this project. A detailed feasibility study is being carried out.
Preferred Mode of Cooperation: Know-how transfer, equipment supply, technical assistance, strategic business alliances, turnkey arrangement and training.
For more information, contact: General Manager (Agriculture), The Namibia Development Corporation (NDC), Private Bag 13252, Windhoek, Namibia. Tel: +264 61 206 9111; Fax+264 61 233 943

IRRIGATION PUMPS

A well established manufacturer of positive displacement borehole pumps, general industrial pumps and hand pumps, is seeking to upgrade its current production technology. The equipment required includes stainless steel precision cutting, a 4 dimensional milling machine and CNC lathes. The technology will allow the company to redesign its range of industrial pumps and to move towards a J.I.T. production process. The company will market 80% of its products locally and 20% will be exported.
Preferred Mode of Cooperation: Equipment supply, leasing, R&D contract, technical assistance, R&D consortia and strategic business alliances.
For more information, contact: Chief Executive, Mono Pumps Zimbabwe, P>O.Box 2049, Harare, Zimbabwe. Tel:+263 4 771180/3; Fax:+263 4 771179

REPROCESSING STEEL BARS AND COILS BY-PRODUCTS

A large producer of steel bars and coils, manufactured to international standards, is seeking to extend its current export markets. The company currently manufacture some 1 million tonnes of steel products annually, of which 100,000 tonnes are AISI grade. New technology is required to increase the amount of AISI grade steel products. The company also produce large quantities of by-products and wishes to recycle them to reduce costs. Examples are: iron oxide fines, EAF slag and dust. The company requires new technology and equipment to reprocess these by-products.
Preferred Mode of Cooperation: Know-how transfer, licensing, R&D consortia, subcontracting, equipment supply, technical assistance, strategic business alliances and turnkey agreements.

For more information, contact: Managing Director, Alexandria National Iron & Steel Co., El-Dekhiela, Post Code No. 21537, Alexandria, Egypt. Tel: +20 3 433 8621; Fax+20 3 433 2667. Email: ansdk@ritsec1.com.eg

AUTOMOBILE BATTERIES

A small-scale producer of automobile batteries is currently buying the battery cells and assembling them to produce the complete battery. The company is looking for the technology that will allow them to produce the cells in-house. The finished batteries should be highly efficient and low-cost. Improvements will be required in the effectiveness of recycled parts. The envisaged annual production is sufficient cells to produce 600 batteries for Kenya and the COMESA countries. The company needs modern charge measuring devices and knowledge of alternative electrolyte materials.

Preferred Mode of Cooperation: Know-how transfer, patent licensing, subcontracting, equipment supply, technical assistance and strategic business alliances.

For more information, contact: Proprietor, Siwinga Black Batteries, P.O.Box 28848, Nairobi, Kenya.

SOAP AND CHEMICALS FACTORY

Assistance is required to refurbish a dormant soap and chemicals factory. The factory would utilize by-products from the fisheries, agriculture and mining industries, in the form of tallow, limestone, salt, crop oils, recycled paper, fish oils, etc. The project aims to employ around 50 people, capital requirement is in the region of US$500,000. A detailed study is available on request.

Preferred Mode of Cooperation: Joit-venture and equity participation.

For more information, contact: Managing Director, Fressh Soap (PTY) Ltd., P.O.Box 3661, Windhoek, Namibia. Tel:+264 61 226061; Fax:+264 61 227 182.

KNITWEAR PRODUCTION

An existing knitwear operation wishes to radically improve the quality and rate of their knitwear production. They are seeking to improve their performance in the following areas: sourcing of raw materials, production equipment, knitwear designs, packaging and marketing techniques. To start with they are searching for improved knitting technology and machinery, especially computerized machinery. Expertize for improving product design, production processes and maintenance of the machinery is also required. Initially, the targeted markets are domestic, and neighbouring countries.

Preferred Mode of Cooperation: Know-how transfer, subcontracting, equipment supply, technical assistance and strategic business alliances.

For more information, contact: Managing Director, Kabale Knitwear, P.O.Box 928, Plot 4, Babukika Road, Kabale, Uganda. Tel:+ 256 486 23590.

WAX FLOOR POLISH

There is only one manufacturer of floor polish in Zambia. To broaden consumer choice and introduce competition, a local investor is seeking to establish an independent manufacturing unit for wax floor polishes, mainly using locally available raw materials. Finance, equipment and technical assistance are required for manufacture and packaging. The initial envisaged production quantity is 1,000 tonnes per annum. The product should be long-lasting, offer high quality and durability.

Preferred Mode of Cooperation: Financing, equipment supply, technical assistance, marketing and know-how transfer.

For more information, contact: Director, Mirrorshine Investments, c/o wedaz, P.O.Box 30495, 7 Maluba Road, Chilenje South, Lusaka, Zambia. Tel:+26- 1 234 160

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BRAZIL TECHMART '97

Belo Horizonte (Minas Gerais) Brazil
1 – 3 December 1997

INTERNATIONAL BUSINESS FORUM

Organized jointly by UNIDO (United Nations Industrial Development Organization) and the Federation of Industries of the State of Minas Gerais (FIEMG), BRAZIL TECHMART '97 aims to promote and support the formation of technological and joint venture partnerships between and among enterprises from Brazil, particularly the state of Minas Gerais, and from other parts of the world, particularly Austria, Italy, Slovenia and the Republic of Korea. By putting into focus the technological needs as well as the strengths of enterprises in the Brazilian metal-mechanic, agro-processing and biotechnology sectors, the event aims at forging strategic business partnerships that will promote the competitiveness and growth of these three sectors.

Over 70 Brazilian enterprises seeking technological solutions for company growth and competitiveness will be present at BRAZIL TECHMART '97, as well as trade associations, chambers of commerce, manufacturers associations, research institutes, government organizations, technology transfer agents, development banks and venture capitalists

For further information, please contact:

- Director, Technology Services, Investment and Technology Promotion Division, UNIDO, P.O. Box 300, A-1400 Vienna, Austria. Tel: (43-1) 21131-3693, Fax: (43-1) 21131-6809, E-mail: opadicka-kudi@unido.org
- The National Project Coordinator, Brazil Techmart '97 Minas Gerais, FIEMG (Industrial Federation of the State of Minas Gerais), Av. Do Contorno 4520 - 10th floor, CEP 30110-090 Belo Horizonte, Minas Gerais, Brazil. Tel: (0055-31) 229 6645/229 6565; Fax: (0055-31) 239 4636; e-mail: fiemg@fiemg.com.br

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INTECHMART PAKISTAN'97

Karachi, Pakistan
7 – 10 December 1997

INTERNATIONAL BUSINESS FORUM

Organized jointly by UNIDO (United Nations Industrial Development Organization), UNDP (the United Nations Industrial Development Programme) and the Federation of Pakistan Chambers of Commerce and Industry (FPCCI), the Board of Investment, Government of Pakistan (BOI) and the Export Promotion Bureau, the Government of Pakistan (EPB), the INTECHMART PAKISTAN '97 is the first programme to facilitate investment and technology transfer to be held in Pakistan. This programme aims at supporting development of small and medium sized industries by identifying opportunities for selected projects for investment, transfer of technology from abroad, and the transfer of indigenously produced technology overseas. Priority industrial sectors for INTECHMART PAKISTAN '97 are:

- Agro-based industry
- Leather and leather products
- Mineral processing and petrochemicals
- Textiles and garments
- Light engineering and information technologies
- Infrastructure
- Tourism, including hotels and amusement parks

The event will also include a number of workshops and seminars on issues such as technology transfer, project negotiation, use of the Internet to attract investment, intellectual property rights, etc. A conference will also be held on the subject of Investment Policy and Climate in the Country.

For further information, please contact:

- Director, Technology Services, Investment and Technology Promotion Division, UNIDO, P.O. Box 300, A-1400 Vienna, Austria. Tel: (43-1) 21131-3693, Fax: (43-1) 21131-6809, E-mail: opadickakudi@unido.org
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