Polyolefin innovations & new catalyst systems

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Slide 0: Title

The title selected for today’s paper is “Polyolefin Innovations & New Catalyst Systems”.

The polyolefin industry is changing continuously. This development is motivated by the need to further improvement, and thus, to enhance the value of the products that can be produced. It is a change strongly supported by our customers the real beneficiaries.

Ziegler-Natta catalysts have been prominent in the polyolefin market for more than 40 years, but now there are new participants - such as metallocenes. In the face of this new competition, Ziegler-Natta catalysts have not quit, but have instead been reborn through the launch of their own new advanced systems. As you will see in the following presentation, these new Ziegler-Natta catalyst systems have enormous potential.

The polypropylene and polyethylene industries are dynamic businesses, driven by innovation. It is important to remember, however, that their ongoing growth is not simply a result of innovations in the catalysts alone. Their success is a result of continuous innovations in both catalysis and process platforms. As a result of this close association between the process and the catalyst, leading polyolefin manufactures have been at the forefront of catalyst research. Because catalysts behave very differently in different process systems, customization is needed to optimize performance. Therefore, it is essential to have a thorough understanding of both the process technology and the catalyst if these new systems are to be commercially successful.

Slide 1: Topics

Before entering into details regarding some of the latest advances in polyolefin catalysts, I’ll summarise the current state-of-the-art of Ziegler Natta catalyst systems and the driving forces motivating companies to consider catalyst changes. Basell and our predecessor companies have, since the inception of the industry, been leaders in this innovation process, so I’ll describe briefly our current areas of focus and introduce Basell’s Avant range of catalysts for both PP and PE. There is not sufficient time to cover all Avant catalyst systems today, so I’ll focus on a few of our most recent developments, which I believe are very interesting.
I’ll begin with the phthalate family of polyolefin catalysts, which have evolved into a high yield / high selectivity fourth generation catalyst. Then I’ll introduce the new diether and succinate catalysts that are truly revolutionary in terms of ability to tailor make the desired resin property profile. I’ll also talk briefly about how to select the best polypropylene catalyst depending on your resin requirements. Finally, I will introduce our new Z 501 Ziegler HDPE catalyst, which is used to produce PE 100 pipe grades in Basell’s Hostalen process.

**Slide 2: State-of-the-art/ why change?**

Most polypropylene catalyst systems in commercial use today are based on technology developed and introduced in the 1980’s. Different versions are used in a variety of processes to produce a wide range of products. These catalysts are commonly referred to as 4th generation Ziegler-Natta catalysts. Most are titanium based, on a MgCl₂ support. They exhibit good activity and reasonable control of stereoregularity and molecular weight.

So we can ask the question, if existing catalysts are so good, why should anyone change? Especially considering the risks.

Clearly there are many reasons not to change catalysts. Switching catalysts can dramatically change the operational performance of a plant as well as the products produced – for better or worse. Industrial trials take time and require resources. Often large volumes of off-spec material are produced. Many customers require re-qualifications when catalysts are changed, and this sometimes results in lost business.

But while there are risks in changing catalysts, there can also be rewards – specifically the opportunity to enhance the value of the products. The new, most advanced catalysts are able to enhance value by producing new, improved polyolefins with expanded properties. These advanced polymers have better performance, enabling new applications to be targeted. Economics is a consideration, but in reality the cost of the catalyst is only a very small cost in the production of polypropylene. There is a much greater opportunity to realize value by upgrading product capability than reducing catalyst costs. Never the less, costs cannot be ignored, and savings are always welcome by the customer.

The key to a successful catalyst change is proper planning. Catalyst performance in industrial plants is different compared to the laboratory, and performance varies from plant to plant. The risks can be reduced, however, if catalysts are first evaluated in pilot or semi-industrial units. For this reason, Basell operates four pilot plants in addition to industrial manufacturing sites, including our joint ventures, in 18 countries.
Slide 3: Topics - Basell and Avant catalysts

Let me now discuss Basell and our Avant catalyst range.

Slide 4: Basell process & catalyst integration

Basell Polyolefins is a global leader in the development and commercialisation of polyethylene and polypropylene process technologies and related catalyst systems.

The primary process technologies in use in polyolefins today include slurry, bulk and gas phase systems. Basell has developed and actively licenses processes in all three of these technology sectors.

Spheripol process - The most widely used technology for the production of PP homopolymers, random and heterophasic copolymers.
LIPP - Bulk, stirred-vessel technology for homopolymer PP production.
Spherilene and Lupotech G - Gas-phase process for the production of LLDPE and HDPE.
Hostalen - Low-pressure slurry process for unimodal and bimodal HDPE.

Basell catalyst families include:

High yield, highly stereospecific, Ziegler-Natta titanium catalysts for PP production
Ziegler titanium catalysts for PE
Chromium catalysts for HDPE
Metallocene catalysts for PP production

This powerful combination of leading process technologies, advanced catalyst systems, and direct operational experience provide important synergies. A complete understanding of the cause and effect between catalyst and process is essential. Basell is in the unique position of being the leader in all three, and thereby offers added value in our catalyst range.

In 2001, Basell introduced the Avant family of catalysts. Avant is the trade name for Basell’s most advanced catalyst systems, and is comprised of four families of catalysts:

Avant ZN – Ziegler Natta catalysts for the production of PP homopolymers, random and heterophasic copolymers
Avant Z – Ziegler catalysts for the production of HDPE and LLDPE
Avant C – Chromium catalysts for the production of HDPE
Avant M – Metallocene catalysts for the production of PP, and in the future also for the production of PE

**Slide 5: Basic principles of Avant Catalysts**

Production of Avant ZN catalysts begins with the preparation of a magnesium chloride carrier, or support as it is often called. Following the preparation of the base support, the active titanium component is added to the support together with an internal electron donor. The selection and use of an internal electron donor is essential for the performance of the catalyst.

**Slide 6: Basic principles – role of internal donor**

The internal donor influences both the operation of the process and the range of products that can be produced. Proper selection and use of internal donors can modulate catalyst activity and hydrogen response, and improve polymer mechanical and rheological properties through better control of molecular weight distribution, microtacticity and oligomer content.

Basell devotes considerable R&D effort to the development and use of new and better internal electron donors, and we differentiate our range of polypropylene catalysts by the internal donors used. For example, phthalates and diethers are different internal donors that are used to prepare different families of catalysts. As a result of our successful R&D programs, Basell has broad patent coverage on a number of new systems and is currently the exclusive supplier for many of the most advanced Ziegler Natta catalysts.

**Slide 7: Basic principles - usage**

Avant ZN catalysts are used by polypropylene producers together with an activator, typically an aluminium alkyl, and an external donor. The role of the external donor is similar to the role of the internal donor, and allows fine-tuning of the stereospecificity control. Avant ZN diether catalysts can be used without an external donor, which gives them exceptionally high mileages.

**Slide 8: Avant ZN Range**

Several families of Avant ZN catalysts are available for use in most process technologies. Some are multipurpose, used for the production of a wide range of standard grades, while others are designed for more specialised, higher value, applications. Details will follow on each of these families.

**Slide 9: Catalyst requirements**
As mentioned earlier, Avant ZN catalysts are customized for each process technology. For example, different technologies use different type reactors with different residence times, so catalyst decay (or catalyst life) is adjusted for each.

Particle size and shape is controlled to optimize plant operation, additive mixing and extruder power consumption.

When producing copolymers, it is important to keep the sticky rubber phase away from the particle surface to prevent reactor fouling or handling problems. By adjusting the catalyst porosity, the rubber phase can be formed inside the particle.

High yield catalysts can improve plant economics as well as product quality. Stereoregularity expands the range of products through better control of crystallinity, while increasing hydrogen sensitivity expands the range through better control of polymer molecular weight. Increasing bulk density can increase the throughput of the plant, and some catalysts, such as diethers, permit the elimination of external donors for certain products, which simplify operation and reduce costs.

Slide 10: Topics – Phthalate catalysts - evolution

Now I would like to discuss each of Basell’s three Avant ZN catalyst families. I shall begin with the phthalates, which can be considered to be an evolutionary type of catalyst family.

Slide 11: What is a phthalate catalyst?

Phthalates, besides being difficult to pronounce, are organic chemicals that are readily available in the market.

Avant ZN, 4th generation, high performance, phthalate catalysts are multipurpose catalysts designed to economically produce a wide range of products. These catalysts use phthalates as internal donors. They have good morphological control and are widely used in film, fibres, injection molding, and other applications.

The size and shape of the catalyst particle influences the size and shape of the polymer particle. Here is an electron micrograph of a few Avant ZN phthalate catalyst particles. As you can see, the particles are very spherical and uniform, which produce ... very uniform spherical polymer particles.

Proper control of catalyst and polymer morphology is important for plant operability, product handling and product quality, as mentioned previously.
Avant ZN phthalate catalysts produce PP with a very narrow particle size distribution. The amount of fines (say sub 75 microns), which under certain circumstances can cause operational problems, is very low.

**Slide 12: Avant ZN series catalysts - drop-in capability**

This graph shows the matching of the hydrogen response of Avant ZN phthalate catalyst to other phthalate based catalysts. These catalysts can produce polymers in the range from fractional up to about 30 MFR directly in the reactor. In other words, the same range of products can be made with these new catalysts as with existing phthalate catalyst systems. So the question is - why should you change catalysts?

**Slide 13: Phthalate activity**

The answer lies within this graph. The Avant ZN phthalate catalysts typically have ca. 40 % higher yield depending on the MFR. The catalyst yield is typically 60 t/kg for a reactor residence time of around 2 hours. What this means is reduced catalyst and donor consumption, and the possibility to reduce the additives level in the polymer due to the lower catalyst residues.

ZN111 is an example of a Basell catalyst that has evolved from standard fourth generation catalysts. These optimised catalysts will continue to play an important role in PP production in the future.

So in summary, if the objective is to improve process economics, while producing existing grade ranges, changing to the new Avant ZN phthalate catalysts makes sense.

**Slide 14: Topics - Diether/ Succinate catalysts - revolution**

Now I would like to discuss Basell’s new catalysts that are revolutionary in that they are designed around new types of internal donors. These fifth generation catalysts offer previously impossible control of polymer properties.

**Slide 15: What is a diether catalyst?**

Diethers include original novel chemicals designed by Basell R&D following extensive molecular screening.

Avant ZN diether catalysts use diethers as internal donors, and are known as 5\(^{th}\) generation catalysts. The discovery by Basell of diethers as an internal donor was a breakthrough which:
Increased mileage – Improving plant performance
Improved hydrogen response – Expanding product capability by allowing for the production of very high melt flow grades
Produced narrow MWD – Needed for speciality fibre and TWIM grades

Like the Avant ZN phthalate catalysts, the diethers are also produced to be very spherical with a narrow particle size distribution. The resultant resin produced mirrors the original catalyst particles being very regular in shape, with low fines and good powder flowability.

**Slide 16: Diether activity**

Yield is one the most important attributes for PP catalysts, and Avant ZN diether yield is roughly double compared with current 4th generation catalysts. Expanding on the yield graph shown earlier with the Avant ZN phthalate catalysts, you can see that diether catalyst yields above 100 tons/kg can be achieved with 2 hours residence time. In addition, diether catalysts do not require the use of external donors for many grades. However, to achieve highly isotactic polymers, external donors can be employed which slightly depress the yield as a trade off against the higher xylene insolubles.

**Slide 17: Diether xylene insolubles**

Expanding on this, low xylene soluble levels, 2-4%, can be achieved without external donors. Highly isotactic products, up to 99%, can be produced with the use of an external donor. These highly isotactic products exhibit exceptional stiffness, in excess of 2000 mPa, and can be used in film applications where good barrier properties are required, as well as in TWIM applications requiring high rigidity.

**Slide 18: Diether H2 response**

Avant ZN diether catalysts have exceptional hydrogen response. Higher hydrogen sensitivity requires less hydrogen for equivalent melt flow rate polymers, which results in lower amounts of oligomers.

As this chart shows, diether catalysts produce resins with MFR’s of around 1 order of magnitude higher compared to standard 4th generation catalysts at the same hydrogen concentration.

Very high fluidity homopolymers, in excess of 1000 MFR, can be produced directly in the reactor, eliminating the need for peroxide for visbreaking. These resins are used effectively in melt blown fibre applications, as will be explained later.
High melt flow rate heterophasic copolymers with MFR's over 100 can also be produced without visbreaking. The high fluidity of these grades makes them ideally suited for Thin Wall Injection Moulding (TWIM) applications. These products also exhibit superior mechanical balance, because eliminating visbreaking allows a re-balancing of the matrix and the rubber phases.

Narrow molecular weight distribution homopolymers can be produced with polydispersity indices of 3 – 3.5 for spun bond fibre applications, while narrow molecular weight distribution random copolymers exhibit excellent impact resistance at sub-zero temperatures.

For the sake of illustration, here are some pictures showing the applications wherein diether catalyst based resins are used...

**Slide 19: Diether non-woven applications**

Firstly, for non-woven applications where good adsorption is required or for hygienic applications, diether based resins show clear advantages. The very uniform MWD allows the converter to make low denier fibres, thereby enhancing the adsorption or filtration capacity. Alternatively much higher spinning speeds at the same denier can be achieved, which represent cost savings for the converter. Furthermore, the reduced or eliminated peroxide requirement means that the organoleptic (taste and smell) characteristics of these resins are much superior.

**Slide 20: Diether melt blown applications**

This slide shows a conventional 4th generation resin that has been produced with peroxide visbreaking, versus an 1800 MFR diether homopolymer resin produced without peroxide. The photos clearly show narrower and more uniform fibre diameter of the diether resin. The narrower fibre diameter distribution, in combination with the finer fibres, is very useful in filtration applications, where the smaller and the more uniform pore size distribution play an important role.

**Slide 21: Diether TWIM applications**

Finally the thin wall containers shown are all moulded from a 100 MFR diether heterophasic copolymer without visbreaking. These resins have an exceptional stiffness-impact balance, being far superior to normal resins of this MFR. This combination allows reduction in wall thickness, which in turn reduces part weight and polymer usage, ultimately providing cost savings. Higher flow means faster mould filling, increased parts per minute production and design flexibility.
By the way, most products presented are commercially available Basell resins that have been produced on our commercial plants in North America or Europe, and are marketed under the Moplen and Pro-Fax Ultra brand.

So if we ask the question again, why would anyone consider changing to an Avant ZN diether catalyst? The answer is, to expand product capability, improve product quality and enhance operational performance.

**Slide 22: Topics – Diether/Succinate catalysts - revolution**

The latest addition to the Avant ZN catalyst family is our new **succinate** catalysts. This past May, Basell issued a press release announcing the launch of this new family of catalysts. These catalysts are currently produced in Ferrara, Italy. They have been extensively tested in laboratory and pilot plant facilities, and have recently been demonstrated on commercial LIPP and Spheripol plants. They are expected to be in regular commercial use around the end of this year.

**Slide 23: What is a succinate catalyst?**

Succinates are derivatives of succinic acid and, like diethers, include original novel chemicals designed by Basell R&D following extensive molecular screening.

Basell’s Avant ZN succinate catalysts use succinates as internal donors, and are the latest advance in 5th generation catalyst systems. The discovery by Basell of succinate as an internal donor was a revolutionary breakthrough for the production of broad MWD products.

Like the Avant ZN phthalate and diether catalysts, the succinates are also produced to be very spherical with a narrow particle size distribution. The resins produced with these catalysts mirror the original catalyst particles and are very regular in shape, with low fines and good powder flowability.

**Slide 24: Succinate general characteristics**

Homopolymers produced with Avant ZN succinate catalysts are characterised by the following:

High isotacticity with broad MWD
High stiffness injection molding grades – In mono-modal operation, the same stiffness as commercial bi-modal grades is obtained, but with a narrower MWD which improves polymer processability and output
Pipes – Processability is improved with better physical properties
BOPP – Improved cost/performance
In heterophasic copolymers, injection molding applications exhibit improved stiffness / impact balance.

**Slide 25: Succinate catalysts - superior HECO balance**

As you can see from this slide, heterophasic copolymers produced with succinate catalysts offer unprecedented impact/rigidity balance compared to traditional phthalate based resins. The combination of the broad MWD and the highly crystalline matrix, mean that the stiffness of these resins is very high without external nucleating agents.

So, again we ask the question, why would anyone consider changing to an Avant ZN succinate catalyst? The basic answer is the same as for diethers, but for clearly different (product property) reasons - to expand product capability, improve product quality and enhance operational performance.

**Slide 26: Topics - Catalyst selection**

So which catalyst should you use? As we have seen this depends on the process technology in use and the products to be produced.

**Slide 27: Catalyst selection - homopolymers**

In this chart, each of the major homopolymer PP applications are listed according to the typical composition requirements of the products. Phthalate catalysts, used in mono-modal process technologies, produce standard, commodity oriented, polypropylene grades.

Diether catalysts expand the property envelop, enabling the production of higher value, speciality, fibre and TWIM grades requiring narrow molecular weight distribution.

Succinate catalysts expand product properties in the opposite direction of diethers, broadening the MWD, which is useful to improve stiffness for applications such as pipes, BOPP and injection moulded grades. Succinate catalysts enable broad MWD products to be produced in single reactor systems. Traditional catalysts require dual reactors to produce similar “bi-

Use of multi-modal process technologies, such as the Spheripol process, enable the molecular weight distribution to be further broadened, expanding the product range of all catalyst systems, especially succinates.
Slide 28: Catalyst selection - copolymers

If copolymers are to be produced, we can do the same analysis considering the desired applications and typical composition requirements of the products.

As in homopolymers, phthalate catalysts, used in mono-modal process technologies, can produce most standard copolymers.

Diether catalysts expand the property envelope through their ability to produce products with a narrower molecular weight distribution and high melt flow, opening the door to high melt flow heterophase copolymers, while succinates broaden the MWD and increase stiffness.

Again, use of multi-modal process technologies, such as the Spheripol process, enables the molecular weight distribution to be further broadened, expanding the product range of all catalyst systems.

Slide 29: Avant ZN catalysts- summary

In summary, if new catalyst systems are to be “commercially” successful, it is essential to also have a thorough understanding of the process and the products to be produced. There are risks in changing catalysts, that should not be underestimated, but there may also be rewards, especially if product capability can be expanded. Different catalyst families, based on different internal electron donors, have different performances and product capability. Avant ZN new 4th generation phthalate catalysts are drop-in replacements offering economic advantages. Avant ZN 5th generation diether catalysts extend the property profile to include high MFR, high crystalinity and narrow MWD resins. Avant ZN 5th generation succinate catalysts produce broad molecular weight distribution resins with improved stiffness and processability. Basell is uniquely positioned as the leading process licensor, PP producer and catalyst supplier, and has over 35 Avant ZN catalysts, designed for use in most technologies including bulk, slurry and gas phase systems.

Slide 30: Topics – Avant Z 501 catalyst for PE 100 pipe grades

Before concluding, I would like to briefly discuss PE 100 pipe applications produced with Avant Z 501 HDPE catalyst.

Slide 31: Avant Z 501 - PE 100 pipe application

Basell has developed, and actively licenses, the Hostalen low-pressure slurry process for uni-modal and bi-modal HDPE. The powerful combination of Hostalen cascade process technology, with the advanced Z 501 catalyst
system, provides tailoring of HDPE product properties by tailoring the molecular mass distribution and co-monomer distribution.

Avant Z 501 catalyst, in cascade mode operation, produces a very low molecular mass homopolymer with high crystallinity in the first reactor, which is the basis for very good processability of the polymer and a high stiffness of the HDPE product. In addition, the very high molecular mass copolymer, with low crystallinity, produced in the second reactor is responsible for the high impact strength and stress crack resistance. Due to this “in-situ” blending in polymerisation, the resin shows a broad or bimodal molecular mass distribution and an inverse co-monomer distribution. This combination results in excellent melt flowability and long term hydrostatic strength or strain hardening.

**Slide 32: Avant Z 501 - PE 100 pipe application**

PE 100 pipe is a good example of a successful development of an advanced application though innovations in both catalysis and process systems. Avant Z 501 catalyst, when used in the Hostalen process, is capable of producing a wide range of products including injection molding, functional packaging, tapes & monofilaments, and pipes. One of the more sophisticated applications coming from this catalyst is for pipes, including PE 80 and high pressure PE 100. High stiffness, excellent toughness, very good stress crack resistance, and good processability characterize these products. Basell’s PE 100 resins demonstrate an outstanding combination of mechanical properties, which is the key to entering into new high-pressure applications like gas distribution pipes and water pipelines.

**Slide 33: Topics - Conclusions**

Due to time limitations, I have only introduced a few of Basell’s polyolefin technologies.

**Slide 34: Conclusions**

Never-the-less, it should be clear that Basell has played an important role in the evolution of the polyolefins industry through the development of new polypropylene and polyethylene catalyst systems and process technologies, and we expect our new revolutionary systems will continue to shape the future of this industry.

**Slide 35: End**

Thank you for your attention.
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