METALLOCENE TECHNOLOGY

in Commercial Applications
# Metalloocene Catalysts Initiate New Era In Polymer Synthesis

## Catalyst Evolution Timeline

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</thead>
<tbody>
<tr>
<td>Low-density polyethylene</td>
<td>• Linear PEs&lt;br&gt;• Primarily high-density</td>
<td>• Linear PEs&lt;br&gt;• High-and-low-density</td>
<td>• First generation&lt;br&gt;• Controlled-architecture PEs: linear to bimodal&lt;br&gt;• Tailored performance: improved properties and/or processing&lt;br&gt;• Principally low- and very low-density</td>
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**Bimodal Catalyst**
- Competitive product performance in single-reactor platform

**Next generation**
- Extend density range
- Improve product performance
- Extended applications

**Bimodal Catalyst**
- Broaden application areas
WHAT IS SPECIAL ABOUT METALLOCENE CATALYSTS....

• Why did the industrial research focus on the metallocene catalyst research?
• Why were so many industrial research organizations willing to invest such a huge amount in this research?
Some of **Main Factors** that influenced the research spending in this area are:

1) *High productivity of the catalyst*
2) *Narrow molecular weight distribution (MWD)*
3) *Better Comonomer Distribution (CD)*
4) *Better tailoring of the resin*
1) **High**

Productivity of the catalyst

Higher productivities for catalysts translate to lower catalyst cost and cleaner polymer.

A comparison of the PE produced with metallocene, Ziegler-Natta and chromium catalysts.
2) **Narrow**

Molecular Weight Distribution (MWD)

- Metalloocene catalysts gives narrower MWD than the other two catalyst systems.
- Metalloocene polymer has less low-molecular weight and narrow than other polymers. This reduces the smoke, taste, contaminate but process will difficulties.
- Due to metalloocene polymer contain higher amount of high molecular weight fraction. The reasons why metalloocene resins have better properties than Ziegler-Natta and chromium resins.
3) **Better**

**Comonomer Distribution (CD)**

- The metallocene catalysts have greater efficiency in using comonomer to reduce the density.
- Metallocene catalysts require *less comonomer* to achieve the same density and that in turn reduces the production cost of the low-density polymer.
- This is one of the reasons why all the companies involved in the metallocene catalysis introduced low-density polymer first to the market.
4) Better
Tailoring of the resin

- Metalloocene catalysts are capable of producing polymer with varying molecular weight and comonomer incorporation.
- Bi-modal polymer form metalloocene will have better processing through molecular weight segregation and better properties through comonomer segregation.
- Metalloocene catalysts are capable of producing homo and copolymers that were economically unfeasible before.
- Polymers and copolymers of cyclic olefins are good examples of such polymers.

*Ability to control polymer molecular architecture, allowing independent manipulation of key parameters;*
- Molecular Weight Distribution (MWD)
- Comonomer Distribution (CD)
- Long Chain Branching (LCB)
- CD with respect to MW
Broad Platform of Products

Products span the range of olefinic properties and deliver a world-class set of attributes to add value to your application.
Various Application from Metallocene Polymers

- m-LLDPE
- m-HDPE
- m-EPDM
- m-PP

MODIFIER

TPOs compound

Rubber blends

EVA Alternatives

PVC replacement
Metalloocene Market Continues to Grow

**Global Metalloocene PE Demand** Thousand tons annually (kta)

- **Global Total**: 9.6%
- **LL – Film**: 9.5%
- **LL – Other**: 8.8%
- **HD**: 12.8%

Source: Nexant ChemSystems, POP8 2009 Executive Report
CONCLUSION

• Metallocenes will revolutionize the polyolefin industry by opening new opportunities that were not accessible in the past.
• Major polyolefin producers will need a strong metallocene program to be able to compete in the future.
• The design of a catalyst system for the manufacture of polyethylene in today’s high capacity world-scale plants to serve volume PE markets is a major and very costly undertaking.
• The catalyst must make the desired product(s) consistently.
• Its signature kinetic profile and process response behavior must fit the production process to ensure reliable operations.
• The catalyst system must deliver practical manufacturing economics.
Introducing

BIOPOLYMER
Conventional Polymer & Biopolymer

Current Feedstocks

- Oil
- Refining
- Chemistry

New Feedstocks

- Crops
- Biomass
- Metabolic Engineering

Molded parts

- Fuels
- Solvents
- Fibers
Production of Polymer & Biopolymer

Sources of Carbon (Feedstock)

Non-renewable Carbon
- Oil and Natural Gas
- Coal
  - New supplies of oil, gas-to-liquid (GTL) processes
  - coal-to-gas (CTG) and coal-to-liquids (CTL) processes

Renewable Carbon
- Biomass
  - Chemical Conversion
  - Biochemical Conversion
  - Thermochemical Conversion

Feedstock (Carbon Source)
(such as Natural Gas, Oil, Corn, Soybeans, Sugar Cane)

↓
Monomer
(such as Ethylene, Propylene, Lactic Acid)

↓
Polymer
(such as Polyethylene, Polypropylene, Polylactic acid)

↓
Package
(such as Bottle or Pouch)
What Are Biopolymer?

**Non-renewable Feedstock**

- Renewable, Not Compostable
  - *e.g.* Bio-PE (PP/PVC), biobased PET, PTT, Nylon 11

**Non-Compostable**

- Petrochemical based, Not Compostable
  - Nearly all Conventional plastics
  - *e.g.* PE, PP, PET

- Not Considered Bioplastic

**Compostable**

- Renewable And Compostable
  - *e.g.* PLA, PHA, Starch blends

- Petrochemical based, And Compostable
  - *e.g.* PBS, PBAS, PBAT, PBAST, PCL, etc.

**Non-renewable (fossil) Feedstock**
Material types – three main groups

The family of bioplastics is roughly divided into three main groups:

1. Biobased or partly biobased non-biodegradable plastics such as biobased PE, PP or PET and biobased technical performance polymers such as PTT or TPC-ET
2. Plastics that are both biobased and biodegradable, such as PLA and PHA or PBS
3. Plastics that are based on fossil resources and are biodegradable, such as PBAT.

Today & The Near Future

**Today**
- New Resins
  - Polylactic Acid (PLA)
  - Polyhydroxyalkanoate (PHA)
- Combination Technologies
  - Starch or Fiber + Polymers
- Modifications of Existing Materials
  - Propanediol (PDO)

**Future**
- Basic Materials from Renewable Feedstocks
- Poly Ethylene, Polyurethane precursors and Polyamide
Structures are described as optical copolymers

- **Isotactic**
  - $T_m = 170^\circ C$

- **Atactic**

- **Di-syndiotactic**

- **Syndiotactic**

- **Optical blocks**

- **Stereocomplex**
  - $>220^\circ C$

- **D-Lactic Unit**
- **L-Lactic Unit**
DuPont Bio-PDO

Bio-PDO is the building block for Sorona® and other products

HO-CH₂-CH₂-CH₂-OH

Combined in a Single Biocatalyst

“Breakthrough in Industrial Biotechnology”

LCA: 10 million gallons of gasoline/yr saved at current capacity

100 MM PPY, Loudon, TN
PDO Monomer

1. Harvesting the corn
   Corn is the first plant to be used heavily in the making of polymers. In the future, plants such as beets, wheat, rice and grass will be used.

2. Getting sugar from the corn
   A form of sugar known as glucose is extracted from the kernel, the starchiest part of the corn. Scientists are working on extracting glucose from stalk and straw, which would reduce the cost of glucose production and bring down the cost of products such as Sorona.

3. The fermenter: Turning sugar into a monomer
   The glucose is fed down pipes into a three-story vat containing genetically engineered organisms, water and some vitamins and minerals.

4. Turning monomers into polymers
   PDO, known as a monomer, is shipped to a polymer plant where it is mixed together, or polymerized, with petroleum-based monomer TPA, or terephthalic acid. The polymer comes out in long strands that are then chopped into pellets.

5. Fibers and fabrics are created
   The pellets are shipped to a textile plant where they are spun into fibers. The fibers go into apparel or carpets. In the future, parts for cars or planes could be made from the Sorona polymer.

Deliver renewably resourced materials made from biomass instead of petroleum with uncompromised product performance

- Pro-Cote® soy polymers
- Susterra™ propanediol
- Selar® VP barrier resins
- Zemea™ propanediol
- Sorona® polymers

...an idea whose time has come
DuPont Bio-PDO

The DuPont Bio-PDO™ Value Chain

DuPont™ Renewably-sourced™ Materials

Sorona® Polymer

Textile Fibers
Carpets Fibers
Auto Interiors
Resins, Packaging, etc.

Direct Applications
Specialty Applications
Elastomers
Stretch Fibers

Cerenol™ Polymers

100 Million ppy

DuPont Brand

Multiple

Sorona® (ABS)

Sorona® (EP)
Biomax® (P&IP)

Susterra™
Zemea™
Cerenol™ (ABS)

Renewable Packaging
- Biomax® PTT resins
- Biomax® TPS thermoplastic starch resins (+ Compostability)
- Silar® VP breathable resins
- Solae® Pro-Cote soy polymer
- Biomax® Thermal Modifier

*Zemea™ & Susterra™ are registered trademarks of the DuPont Tate & Lyle Bio Products LLC
Renewable source Nylon

- Good mechanical, RF & Impact
- Resistance to polar fluids
- Low moisture absorption
- Good paintability, extrudability
- Up to 100% bio-sourced
- Non-food crop sourced

PA10,10
PA 6,10

Fuel lines
Pneumatic tubes
Air brake tubes
Handheld device

Renewable sourcing for long chain polyamides

Castor Oil
Sebacic acid
Diaminodecane
Hexamethylene diamine

PA1010
PA610

100% Renewable Carbon
62% Renewable Carbon
Future – Biobase PE

- Can be made from renewable resources (sugar cane)
- Not bio-degradable
- Same properties, processing & performance as PE made from natural gas or oil feedstocks because molecules are the same.
Application
Use in Automotive market

• Bioplastics are already being used in automobile interiors and in cases for consumer electronics.
• Toyota Motor Corp. became the first automaker in the world to use bioplastics in the manufacture of auto parts, employing them in the cover for the spare tire
• Toyota Motor is building a plant to undertake test production of bioplastic at a factory in Japan, with production due to begin in August 2004.
• The company plans to produce 1,000 tons of bioplastic annually, which will be used not just in car parts but in many other plastic products as well.
• Toyota also plans to use bioplastics in the construction of the exhibition pavilions at the 2005 World Exposition, Aichi, Japan, so that no construction waste is generated when the pavilions are dismantled at the end of the event.
**Used in Electronic Devices**

- Mitsubishi Plastics has already succeeded in raising the heat-resistance and strength of polylactic acid by combining it with other biodegradable plastics and filler, and the result was used to make the plastic casing of a new version of Sony Corp.'s Walkman released last fall.

- Mitsubishi Plastics had previously looked at bioplastic as something that would mainly be used in the manufacture of casings and wrappings, but the company now feels confident that this revolutionary material has entered a new phase in its development in which more complex applications will be found.

- NEC Corp., meanwhile, is turning its attention to kenaf, a type of fibrous plant native to tropical areas of Africa and Asia that is known to grow more than five meters in just half a year.

- A mixture of polylactic acid and kenaf fiber that is 20% fiber by weight allows for a plastic that is strong enough and heat resistant enough to be used in electronic goods.

- The goal is to begin using this new plastic in real products, such as computer cases, within two years.
Use in Packaging

• The use of bioplastics for shopping bags is already very common.
• After their initial use they can be reused as bags for organic waste and then be composted.
• Trays and containers for fruit, vegetables, eggs and meat, bottles for soft drinks and dairy products and blister foils for fruit and vegetables are also already widely manufactured from bioplastics.
Use in Catering products

- Catering products belong to the group of perishable plastics.
- Disposable crockery and cutlery, as well as pots and bowls, pack foils for hamburgers and straws are being dumped after a single use, together with food-leftovers, forming huge amounts of waste, particularly at big events.
Use in Gardening

• Within the agricultural economy and the gardening sector mulch foils made of biodegradable material and flower pots made of decomposable bioplastics are predominantly used due to their adjustable lifespan and the fact that these materials do not leave residues in the soil.

• This helps reduce work and time (and thus cost) as these products can simply be left to decompose, after which they are ploughed in to the soil.

• Plant pots used for flowering and vegetable plants can be composted along with gardening and kitchen litter.
Use in Medical Products

• In comparison to packaging, catering or gardening sectors, the medical sector sets out completely different requirements with regards to products made of renewable and reabsorbing plastics.
• The highest possible qualitative standards have to be met and guaranteed, resulting in an extremely high costs, which sometimes exceed 1.000 Euro per kilo.
• The potential applications of biodegradable or reabsorbing bioplastics are manifold.
Due to their specific characteristics, bioplastics are used as a basis for the production of sanitary products. These materials are breathable and allow water vapor to permeate, but at the same time they are waterproof. Foils made of soft bioplastic are already used as diaper foil, bed underlay, for incontinence products, ladies sanitary products and as disposable gloves.
Question...
Thank you very much
Exposure to Bisphenol A (BPA)
Why are people concerned?

- BPA has been associated with health risks to include brain abnormalities, reproductive system abnormalities, cancer, obesity, heart disease, diabetes, and child asthma.
- A NIH study reported by the Centers for Disease Control and Prevention found detectable levels of BPA in 93% of respondents.
- Early-life exposure to BPA may affect testis function in adulthood.
- Women with polycystic ovary syndrome have higher BPA blood levels.
- Children eating multiple servings per day of canned foods would get a dose of BPA approaching levels that have caused adverse affects in animal studies.
Where is BPA found?

- Baby bottles
- Water bottles
- Canned food and drinks
- Canning lids
Alternatives to BPA

- Plastic alternatives
  - Glass and stainless steel
  - Aluminum paired with a BPA-free epoxy liner
  - Tritan Copolyester™ by Eastman Chemical
  - High Density Polyethylene - #2 plastic
  - Polypropylene - #5 plastic
  - Grilamid TR-90 – a thermoplastic nylon

- Epoxy Resin Alternatives (Can Liners)
  - Polyester Coatings (DAREX Polyester, PET film)
  - Based-On Resins (Oleoresin)
Alternatives: Tritan – High Heat Copolyester

Taking the next steps toward satisfying consumer needs.

Baby steps.

Eastman Tritan™ copolyester provides an important alternative to polycarbonate. The launch of Tritan has transformed the way the industry thinks of clear polymers because of its unique balance of properties:

- BPA-free (made without bisphenol-A)
- Toughness
- Dishwasher durability
- Functional clarity
- Processability
Giant steps.

New Eastman Tritan™ EX401 copolyester addresses health and regulatory issues important to the infant-care market. With this resin, Eastman takes the first steps towards assessing the effects of products in contact with the body. Eastman is using the introduction of Tritan EX401 to lead the industry toward establishing biocompatibility testing protocols for the infant-care market.

Stepping up for you.

Eastman Tritan™ EX401 copolyester also is proof of the commitment Eastman is making to this important and quality-conscious market segment.

- It offers the flexibility of being suitable for extrusion blow molding (EBM) and injection molding (IM).
- Tritan EX401 empowers you to design and produce bottles, pacifiers, breast pumps and other parts with the properties that are preferred in the marketplace.
Staying in step with your requirements and market preferences.

“They grow so fast when they’re young!”

Although Eastman Tritan™ copolyester was only introduced to the infant-care market in late 2008, it has displaced polycarbonate in a wide range of applications. New Eastman Tritan™ EX-401 copolyester creates even greater value for products that must be sensitive to the rapidly growing concerns of regulation and consumer confidence.
<table>
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<tr>
<th>Property</th>
<th>Eastman Tritan™ EX401 copolyester</th>
<th>PC (polycarbonate)</th>
<th>PES (polyethersulfone)</th>
<th>cPP (clarified polypropylene)</th>
<th>Kostrate® terpolymer</th>
<th>Glass</th>
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<tr>
<td>BPA</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
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<tr>
<td>Infant care-specific</td>
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<td>×</td>
<td>×</td>
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<td>Clarity</td>
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<td>Toughness (impact-/shatter-resistant)</td>
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<td>shatter risk</td>
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<td>Dishwasher durability</td>
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<td>Processability/efficiency</td>
<td>fast cycles; lower temperature</td>
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<td>Biocompatibility certification for infant care</td>
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<td>N/A</td>
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**Legend:**
- × No
- ✓ Yes
- ● Excellent
- ○ Very Good
- ○ Good
- ○ Fair
- ○ Poor
Eastman Tritan™ copolyester
Balancing processing and performance properties

**CLARITY** – *balancing lively aesthetics and long-lived performance*
- A high level of light transmittance
- A low level of haze
- High gloss provides vibrant appearance in colored or tinted products

**TOUGHNESS** – *balancing high visual impact with enduring impact resistance*
- Tough
- Durable
  - Maintains functional and aesthetic integrity over product life

**CHEMICAL RESISTANCE** and **HYDROLYTIC STABILITY** – *tipping the balance in your favor*
- Eastman Tritan™ copolyester can withstand many harsh chemical environments without crazing, cracking or hazing

**GLASS TRANSITION TEMPERATURE** – *balancing heat resistance and easy processing*
- Reduced molding and sheet-thermoforming cycle times
- No need for separate annealing step
- Potential for reduced energy use
Features and benefits of Eastman Tritan™ copolyester

**Material features and benefits**

- Very tough
- High Tg (110°C-120°C)
- Excellent clarity
- Chemically resistant
- Hydrolytically stable
- Stain resistant
- Bisphenol-A free
Part name: ECO CUP

- BPA Free
- Toughness, Impact Resistance
- Safe (FDA Approve)
- Heat-resistance (Dish washer safe)
- Chemical Resistance
- Green (Recycle ability)
- Injection process
Part name: Baby Bottle & Baby Product

- BPA Free
- FDA
- Toughness
- Heat resistance
- Won’t retain taste and odors
- Process as normal: Injection, Extrusion Blow Molding.
Part name: Food & Drinking Containers

**BPA-free** Toughness - Impact-resistant, shatter-resistant, stands up to extreme conditions

**Dishwasher safe** - top and bottom rack

Temperature-resistant - Fill with boiling hot liquids or store in the freezer

Odor, taste and stain-resistant

Sparkling clarity and gloss - Molded clear in a rainbow of vibrant colors
Part name: Medical Part

- Inherent toughness helps reduce waste:
  - Less breakage in shipping and handling
  - IV components can be designed with thinner walls.
  - Components may require less packaging.

- Made without BPA or halogens and is not manufactured using ortho-phthalate plasticizers

- Free of chlorine

- Meets hospital Environmentally Preferable Purchasing (EPP) guidelines
  - Bisphenol A (BPA) free
  - No halogens (chlorine, bromine, etc.)
  - Free of ortho-phthalate plasticizers
Actions

- Contact food and beverage companies to advocate the removal of BPA from food packaging such as canned foods and canning lids. Educate them about packaging alternatives.
- Educate your legislators.
- Participate on issues surrounding BPA during the FDA’s public comment period(s) at regulations.gov.
- Tell your friends and family how to limit BPA in their diet.
Thank you very much