
Commercial Perspective on New Developments in Catalysis for Olefin Polymerization

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Presented at
SPE ANTEC
May 1999

ABSTRACT

Olefin polymerization catalysis is a domain of major research activity. For the last decade, much of this research has been focused in the area of metallocene catalysis, which has been at the front line in driving important technology renewal in the polyolefins industry. Developments in metallocene catalysis have instigated much trade press discussion, and now emerging non-metallocene catalyst systems are adding new scope to the industry dialog. Announcements continue to flow in the trade press about the industry's latest new catalyst discoveries. Hetero-substituted cyclopentadiene ligands coordinated with conventional Group IV metals; sterically-hindered, nitrogen-containing ligands coordinated with a variety of transition metal centers, including late transition metals such as Fe, Co, Ni, and Pd; and other heteroatom-based transition metal complexes have been shown to be activated with alumoxanes to form catalytic species that polymerize olefins to various types of polymers. These laboratory developments illustrate, once again, the ever-widening range of catalytic systems for olefin polymerization.

This paper will offer some limited commercial perspective on new catalyst developments using the context of possible business significance to the polyethylene industry. Since some of these developments are barely out of the laboratory, it's pretty early to be writing to provide "commercial perspective" on these systems. The only way that I could conceive to address this subject was to offer some insights on what has been learned from the ongoing development and commercialization of metallocene technology for polyethylene manufacture. I would expect some of these commercialization learnings to anticipate what will be encountered with other new catalyst systems. The commercial perspective I hope to offer will speak both to factors influencing the size of the "commercial prize" and to challenges affecting the timeline for reaching the marketplace and capturing a piece of this "commercial prize."

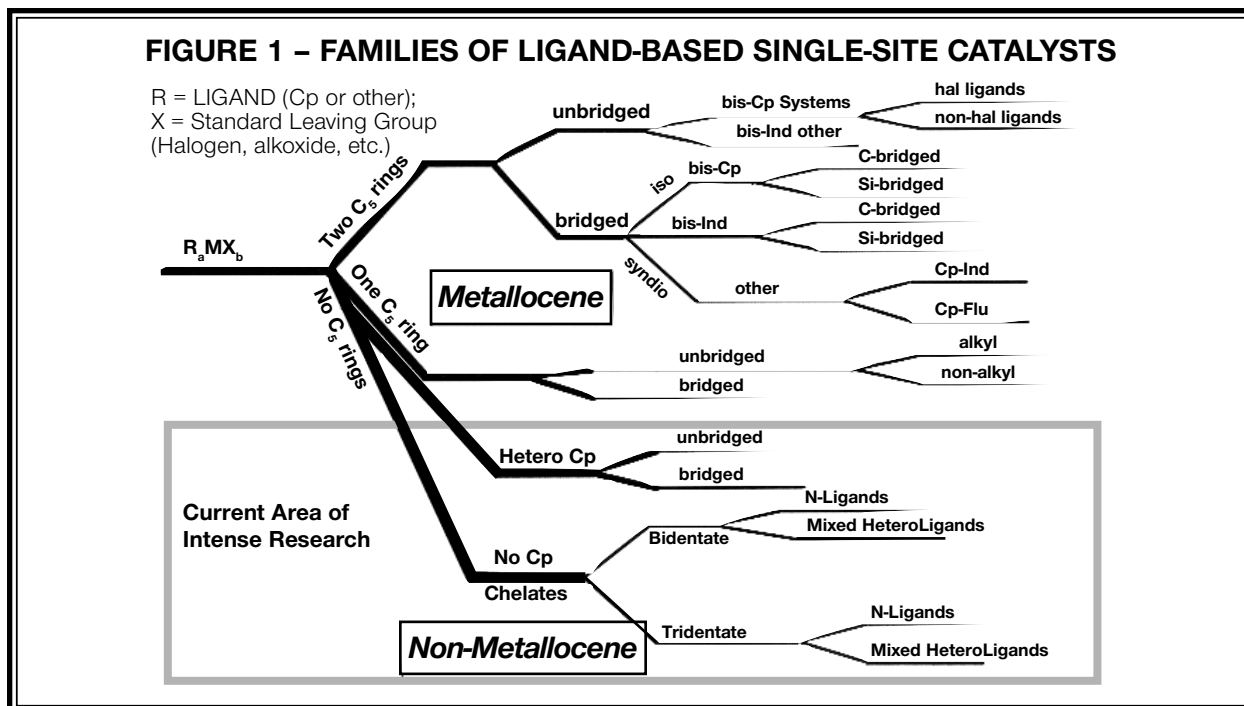
INTRODUCTION

The family tree of ligand-based catalysts is growing. **Figure 1** shows a schematic of this enlarging family tree with new structures moving well beyond the metallocene domain of cyclopentadienyl-containing systems. Symmetric and asymmetric structures, bridged and unbridged, chiral and achiral catalysts are represented. In all these systems, the ligand structure, metal center, and activation chemistry define the electronic and steric environment at the active site of the catalyst and, in turn, establish the catalyst's regulation of the stochastic processes of monomer/comonomer insertion (stereospecific or non-stereospecific) and various chain transfer chemistries.

In **Figure 1**, metallocenes represent one very large, important category of ligand-based catalysts. Metallocene catalysis represents a very broad and very rich technology. There are an enormous number of potential catalyst systems. Some of these catalysts have progressed through the innovation pipeline from research through development to reach the arena of full-scale product commercialization.

The new non-metallocene, ligand-based catalyst structures outlined in **Figure 1** represent, for the most part, developments that are still quite far upstream, inside the innovation process, and are still undergoing laboratory scoping studies. The general capabilities of these new chemistries, let alone their unique capabilities, are not yet fully understood. It will be the unique performance capabilities of these catalysts that will determine their commercial significance to our industry.

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**METALLOCENE CATALYST SYSTEMS —
DEVELOPMENT/COMMERCIALIZATION**

The ongoing development and commercialization of metallocene technology in our industry provides one practical benchmark for conjecturing about the future commercial significance of emerging discoveries in catalysis. The seminal research in metallocene catalysis dates from the mid to late 1970s, with development and prototype commercialization beginning in earnest in the early 1990s. As we end this decade, supply and demand for metallocene-based polyethylenes have become commercially meaningful and show strong growth.

Metallocene catalyst systems are now used commercially in the manufacture of several families of new and improved polymers for both specialty and volume PE markets. The development of these catalysts has been described as a major milestone in the history of polyolefin technology development. Metallocene chemistry, applied to polyethylene production, brings significant product performance enhancements

and applications functionality valued in the resin marketplace as well as significant process technology benefits valued in the manufacturing arena of world scale PE production.

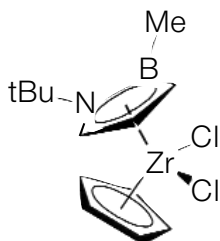
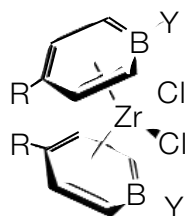
One of the major (and growing) uses of metallocene catalyst systems is the production of linear low-density polyethylene (mLLDPE) using the UNIPOL™ gas-phase process. Production capacity continues to build and demand continues to increase for these new resins. I will use some of this UNIPOL PE experience with metallocene catalysts as a vantage point for attempting to provide commercial perspective on the new catalyst chemistries now emerging from various laboratories.

**NEW NON-METALLOCENE
LIGAND-BASED CATALYST SYSTEMS**

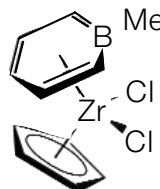
The discovery of new catalyst chemistries for olefin polymerization seems to be a recurrent topic in our industry trade press. The intensity of discussion of metallocene chemistry, its capabilities and implications for the polyolefin

**FIGURE 3 - NON-METALLOCENE LIGAND-BASED CATALYSTS:
HETEROATOM CYCLIC COMPLEXES (CONT.)**

Lyondell, Shell



**Hoechst, Asahi, Dow
Montell, Shell**

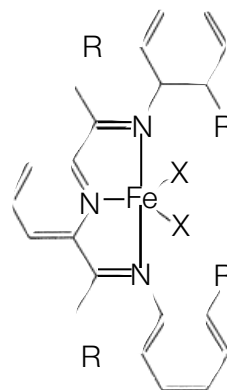
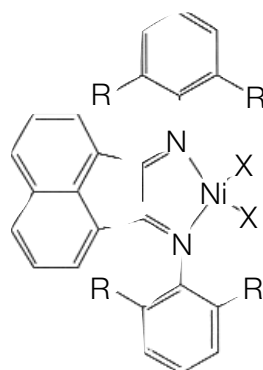
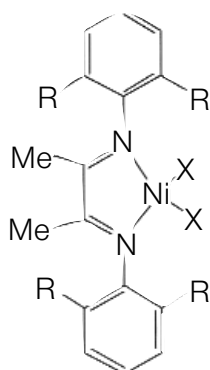
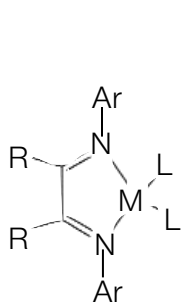


The second group of catalyst precursors shown in **Figure 4** represents a new class of Diimine complexes first introduced by DuPont/UNC. These catalysts are the basis of DuPont's "Versipol" technology. These catalytic systems were revealed in early 1996 with the announcement by DuPont of the filing of a huge patent application containing 562 claims in 503 pages. Shown on the left is the generic precursor formula and on the right are several structural

derivatives that illustrate the richness that the basic nucleus affords. Similar systems based on the bulky Diimine ligands were announced by BP in conjunction with academic researchers at Imperial College. These systems were shown to produce a variety of branched polyolefin structures but appear to be most useful for oligomerizing ethylene to higher α -olefins. Phillips, Exxon, and Eastman also have patents in the Diimine area.

**FIGURE 4 - NON-METALLOCENE LIGAND-BASED CATALYSTS:
DIIMINE COMPLEXES**

Dupont, BP, Phillips, Exxon, Eastman, Union Carbide



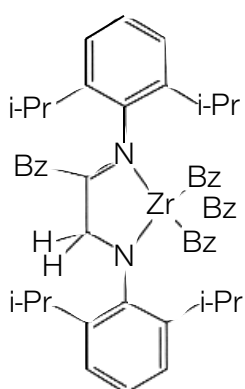
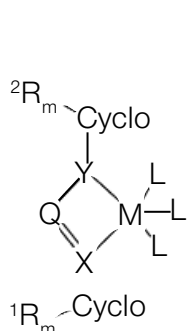
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The third group of catalysts shown in **Figures 5 and 6** is a broad class based on heteroatom chelating ligands, where the coordinating atoms attached to the metals

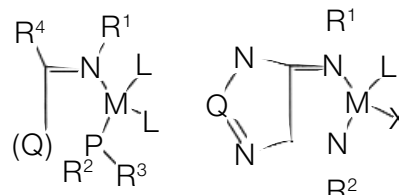
are nitrogen, oxygen, phosphorus, sulfur or mixed atoms. Union Carbide, Eastman, Mitsui and BASF have patented in this area.

**FIGURE 5 - NON-METALLOCENE LIGAND-BASED CATALYSTS:
HETEROATOM CHELATES**

Union Carbide

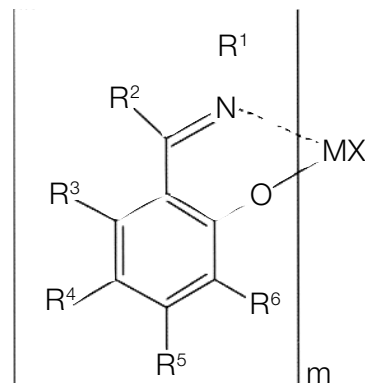
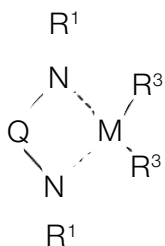


Eastman

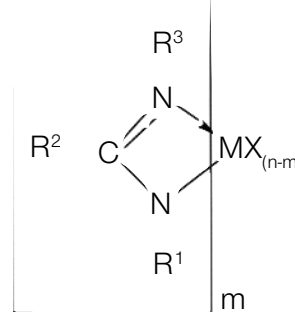


**FIGURE 6 - NON-METALLOCENE LIGAND-BASED CATALYSTS:
HETEROATOM CHELATES (CONT.)**

Mitsui



BASF



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One important aspect of the new ligand-based catalyst developments is the emergence of group VIII or “late” transition metals as active centers. These metals have gone unrecognized as active centers for ethylene polymerization but are widely used in other types of catalytic reactions. Coupled with the fact that these metal centers are tolerant of adjuvants that typically poison standard metal sites, these late metals offer potential for producing olefin polymers of significantly different molecular architecture, including polyolefins containing polar comonomers. Like the catalysts based on hetero-Cp ligands, these new classes of catalysts show varying levels of catalyst activity. Most of these systems appear to be in the earliest stages of development.

The new catalyst precursors shown in these figures continue the recent trend in which the organic ligand structure complexed to the transition metal center plays a dominant role in determining the specific behavior of the catalyst system. The organic ligands in these new systems can be viewed as surrogates for the cyclopentadiene ligands in the metallocene field. Like substitutions to the cyclopentadiene ligand, rational design approaches can be taken to synthesize a wide array of new ligand-metal complexes. Inspection of the generic formulas for the last two classes in **Figures 4-6** really does not give a true indication of the vast number of structures that can be derived from the parent precursor. The suite of possible structures is truly enormous when one considers the array of atoms and connectivity that define the basic structures.

In the catalyst discovery process, researchers must painstakingly work a highly iterative process of manipulating structure to identify the optimum coordination number and oxidation state of the metal and the overall bonding geometry of the complex in order to control the steric and electronic environment that determines the process and product capabilities of the catalyst under polymerization conditions. Application of research tools, such as computational methods and combinatorial chemistry, can help in these pursuits, but

the experimental tasks of synthesizing complexes and measuring their (1) catalytic behavior (activity, kinetics, process responses), and (2) polymer structure manipulation capabilities under laboratory and, then, pilot-scale conditions remain a formidable challenge.

In all modern commercial polyolefin manufacturing processes, catalyst residues remain in the finished polymer. This means that the catalyst system fragments must be completely benign (or made benign) under melt-state shaping conditions and must not cause long-term aging instability problems in the fabricated polymer. As a consequence, commercialization of any new catalyst chemistry also requires investigation of polymer stabilization requirements as part of the technology development protocol. Because the new catalyst chemistries described herein involve new ligand systems and, in some cases, new/unfamiliar (at least for olefin polymerization), late transition metals, special care must be taken to understand the post-polymerization effects (if any) of these residues on resin product performance.

COMMERCIAL FRAMEWORK

The Size of the “Commercial Prize”

The worldwide polyethylene industry is huge and growing. Competition is intensifying. In this industry, new technology creation and development are enormously expensive processes. The business critical mass required to sustain the state-of-the-art technology infrastructure needed to compete in this arena is getting ever larger. The targeted “commercial prize” to justify the technology investments required to convert a new discovery into a commercially practiced technology in this industry must be considered a “big hit.” A “big-hit-technology” means one that can be leveraged across the full critical mass of investing businesses.

The broad commercial success (measured as a return on investment) of any new technology aimed at an existing market accrues from the unique benefits it brings relative to both the incumbent and competing technologies. If the

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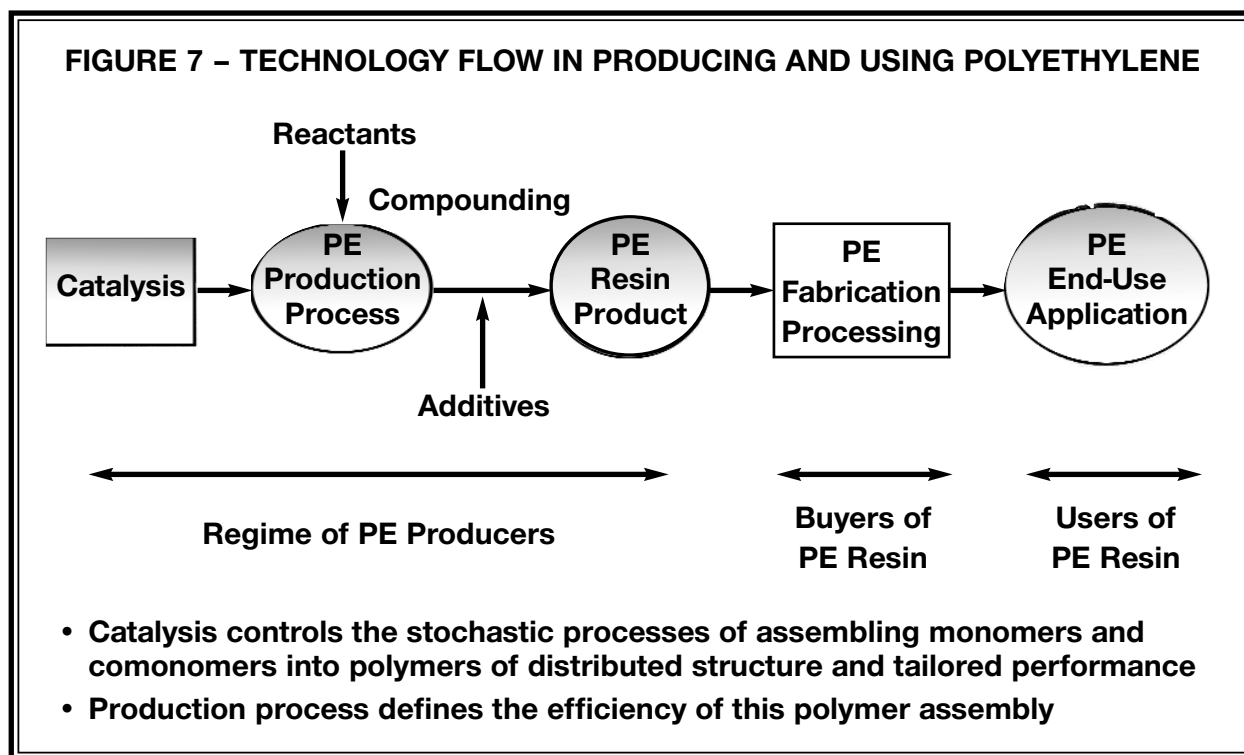
benefits represent simply incremental improvements inside the existing value chain, commercial success will be in jeopardy. The “commercial prize” will be diminished in size and/or its capture will not be achieved.

Specialty mPE and Volume mPE Marketplace Considerations

Catalysis sits far upstream in the technology flow of producing and using polyethylene resins. **Figure 7** presents a concept schematic of this technology flow. Catalysis determines how “mers” are assembled into polymers of distributed structure and tailored performance. The reaction system, i.e., the polymerization process engineering, defines the efficiency of this polymer assembly and the production dynamics of resin manufacture. Process configuration and operating conditions also influence polymer structure, property profile, and end-use performance behavior.

The upstream portion of this technology flow represents the regime of polyethylene producers. Downstream, this technology flow segments into two connected elements of the PE market place: (1) the buyers of PE rein, i.e., the resin fabricators, and (2) the buyers of fabricated goods, i.e., the end-users. In this technology flow framework, catalyst capabilities and performance must be considered from both a supply side, process perspective and a demand side, product/applications perspective.

From a demand side perspective, polyethylenes serve a very broad array of markets and end-uses. They deliver cost-effective value in a wide variety of end-use applications. From pipe and tubing to wire and cable jacketing and insulation to packaging film to bulk containers to thin walled cups and lids, etc., polyethylene products are engineered to deliver very specific sets of performance characteristics. Product functionality in these applications is determined



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by a multi-dimension set of performance attributes that encompasses both end-use physical properties and fabrication processability. These product functionality profiles determine product value in the marketplace. In certain applications, it may be very specific, narrowly-defined “step-out” performance features that determine product value — value that can fall precipitously to zero if certain criteria are not met. At the other end of the spectrum it may be product versatility that defines value.

Metallocene catalysis continues to reveal itself as a shaping force for the future of the polyethylene industry. It is bringing new and better products to a wide range of markets and end-use applications. Its early stage commercialization focus was specialty niche applications; now it is moving into the core of volume PE production and the arena of commodity markets and applications. For specialty markets, the technology development emphasis is on leveraging the molecular engineering capabilities of metallocene catalysts to control with high precision the structure and properties of PE materials tailored for very specific applications. As the technology drives into the volume PE marketplace, process aspects of catalyst performance are rising in the hierarchy of technology criteria for selecting systems to move from development to full-scale commercialization. Throughout the commercial arena (for specialty niche and volume markets), product and process performance consistency are both critical attributes of new technology if it is to

qualify as viable.

In the application of metallocene catalysis to the manufacture of resins with broad product functionality for the volume PE marketplace, economic considerations and manufacturing efficiencies become important drivers of technology development. To win in this commercial arena, metallocene catalyst capability must be integrated with an efficient, cost-effective PE production process.

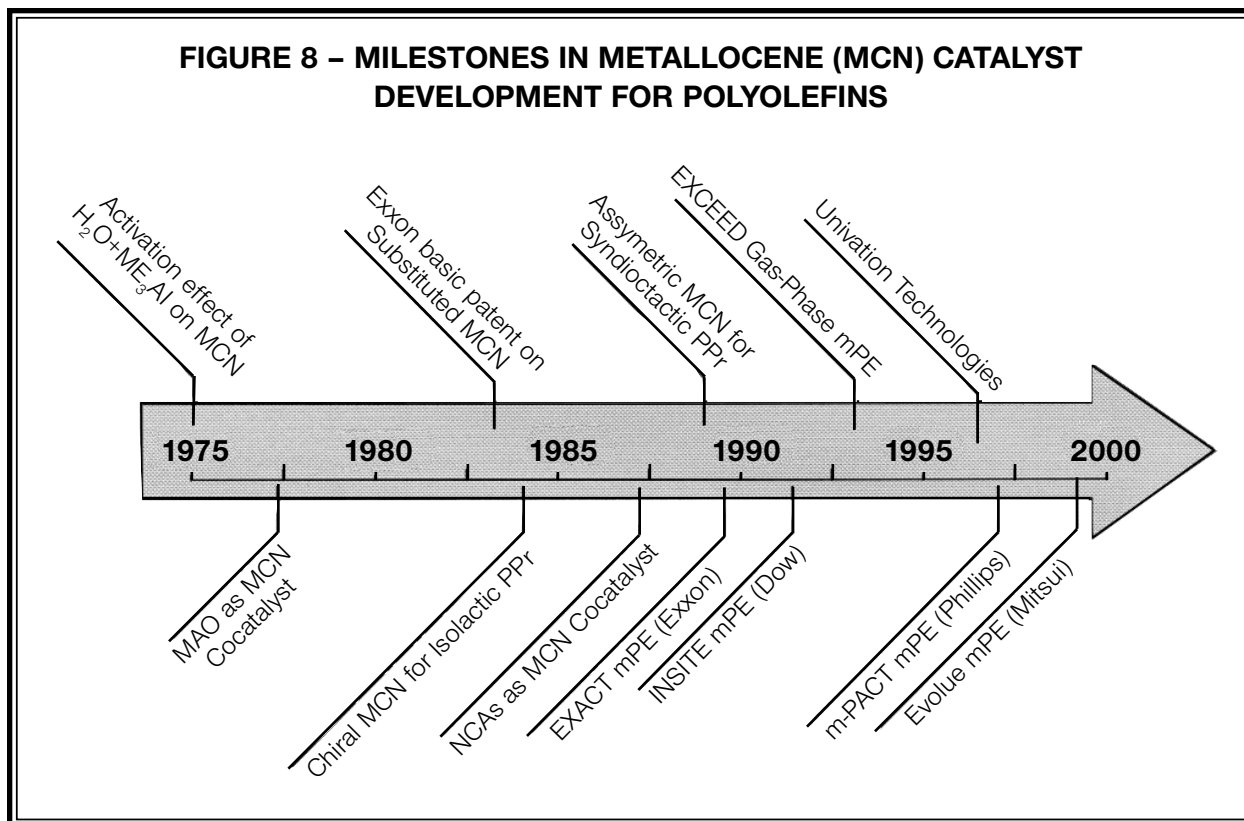
For gas-phase polyethylene production, metallocene chemistry brings important degrees of freedom for tuning catalyst system kinetic behavior and process response characteristics to fit the operating regime of the process. The kinetic behavior of metallocene catalyst systems also plays a key role in polymerization process operability. Specific metallocene systems have been demonstrated to provide a cascade of process technology benefits to UNIPOL™ PE manufacture. The combination of high catalyst activities, unique process response characteristics and control of molecular architecture is being leveraged to further enhance UNIPOL PE manufacturing efficiencies.

THE TIMELINE TO THE MARKETPLACE

The Development Journey

The discovery, development, and commercialization of metallocene catalyst systems for polyolefin manufacture has been a long journey. Selected milestones along this trek are shown in **Figure 8**.

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Since the UNIPOL™ PE process is where I have the most commercial experience with mPE and since this process represents the premier gas-phase process for volume PE manufacture, I will use its operating characteristics as a context for describing the development journey — the overall criteria involved in assessing the commercial viability and business potential of a candidate catalyst chemistry.

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 undertaking. The catalyst must have the potential for making a range of desired product(s) consistently and at high throughput rates. Its signature kinetic profile and process response behavior must fit the production process to ensure reliable, trouble-free operation. The catalyst system must deliver practical manufacturing economics. Additionally, its commercial

implementation must not encompass technology encumbered by the patents of others. Selecting a catalyst chemistry to move from research to development to commercial implementation is a critical business decision, as the costs to achieve full commercialization can be extremely high. A misstep can have a tremendous impact on business timing and, in turn, realized business value.

From Catalyst Discovery to Commercial Practice

The discovery of new catalyst complexes that catalyze ethylene polymerization at high yield is an important first step in a multi-step development process of readying technology for the rigors of commercial implementation in the arena of world-scale polyethylene manufacture. Univation Technologies' R&D efforts employ a holistic systems approach to technology

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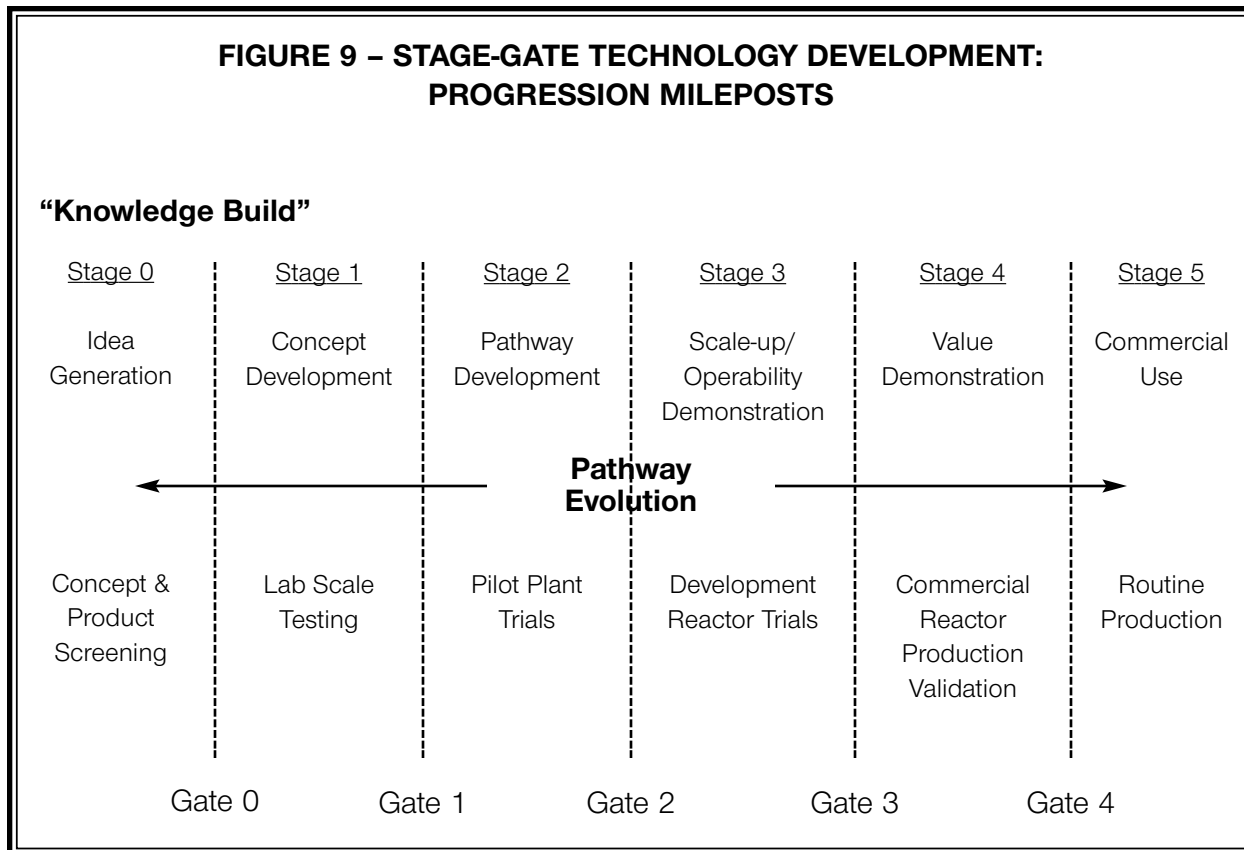
development. Research is progressed from concept evaluation, through development, to commercialization, using a disciplined, comprehensive, iterative, stage-gate work process, which brings a practical, real-world assessment of new technology every step of the way. This development and commercialization process requires strong business commitment, backed by first-principle, technical insights, and real-world understanding to judge the potential of new technology to bring unique benefits and opportunities to the field.

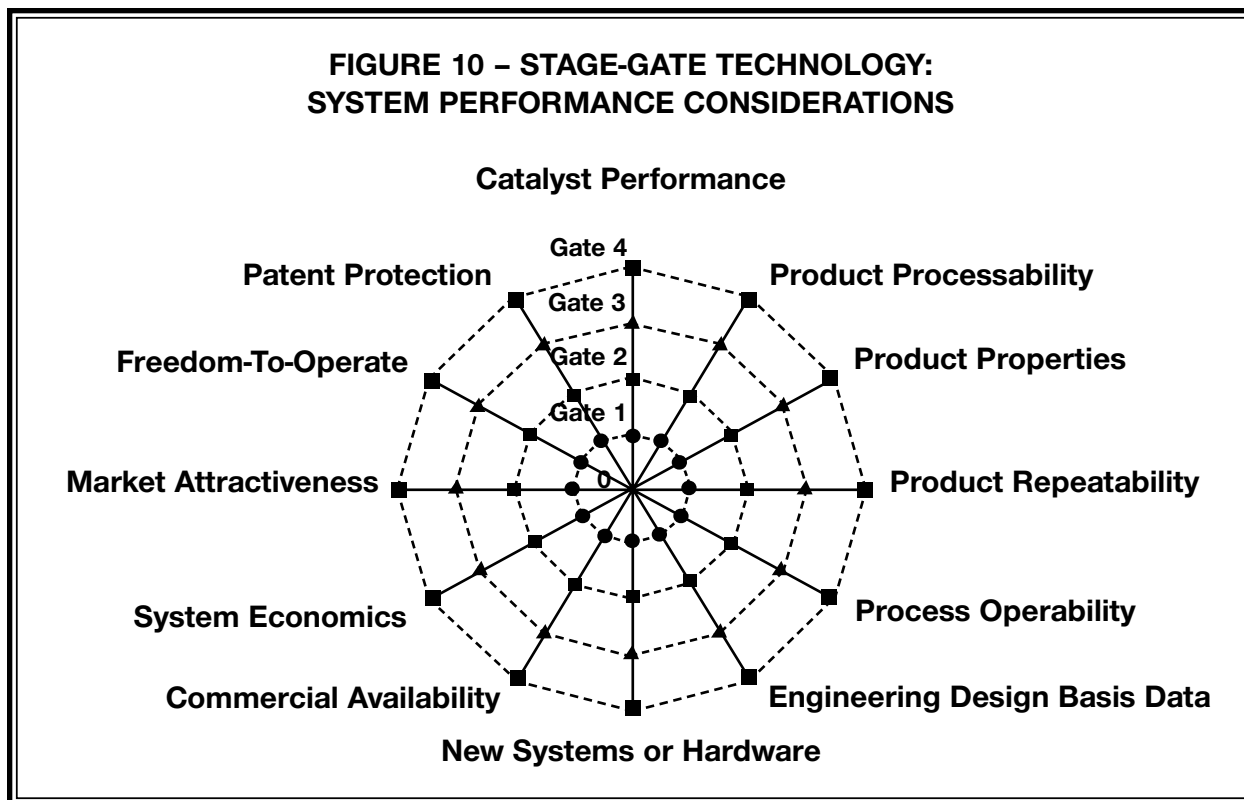
Stage-Gate Technology Development

I would venture that most of the technologists and business professionals in this audience use some sort of stage-gate work process to bring systematized rigor to the naturally chaotic

process of new technology development.

Figure 9 presents a linear schematic of the technology mileposts along the development pathway of progressing a catalyst chemistry from idea — to concept — to scoping studies — to prototype testing — to optimization — to full scale commercialization. Because of the multi-dimension performance considerations that must be addressed in new catalyst technology development, stage-gate thinking is, perhaps, better represented using the radar map or spider plot shown in **Figure 10**. This simple pictorial makes us very aware of the complexity and challenge (think cost) of progressing a new technology all the way to commercial victory and investment payback.



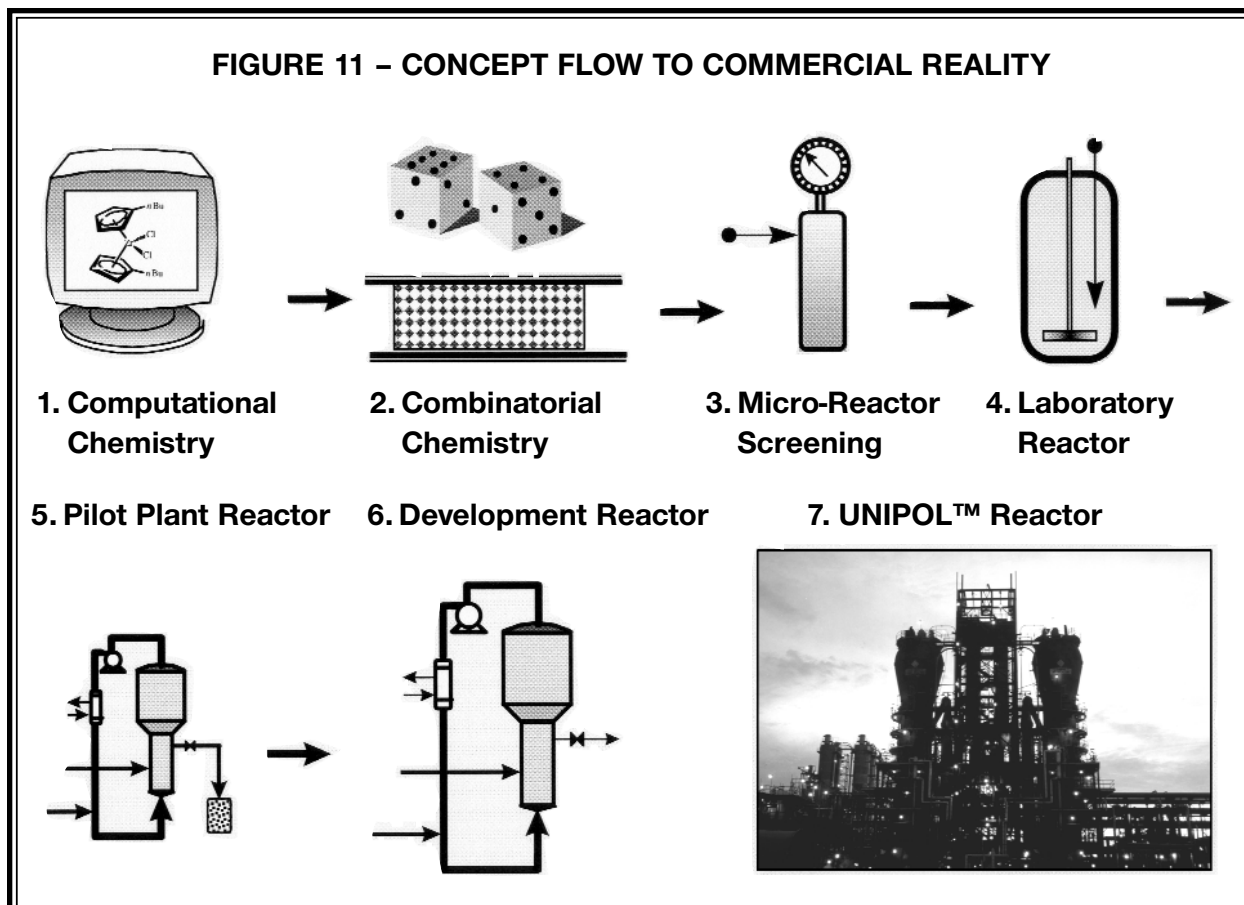


Scale Considerations in Catalyst Technology Development

Research and development in the polyethylene industry is enormously expensive because of the expertise and equipment required to play in the game. **Figure 11** presents a schematic showing the scale and general sequencing of the equipment and facilities used in developing a new catalyst system

for use in the UNIPOL™ PE Process. The top row of bench-scale, laboratory research devices is used to scope candidate catalysts for commercial potential. The bottom row of **Figure 11** shows some of the tools for technology development, optimization, and refinement, and highlights where the “big” money is spent.

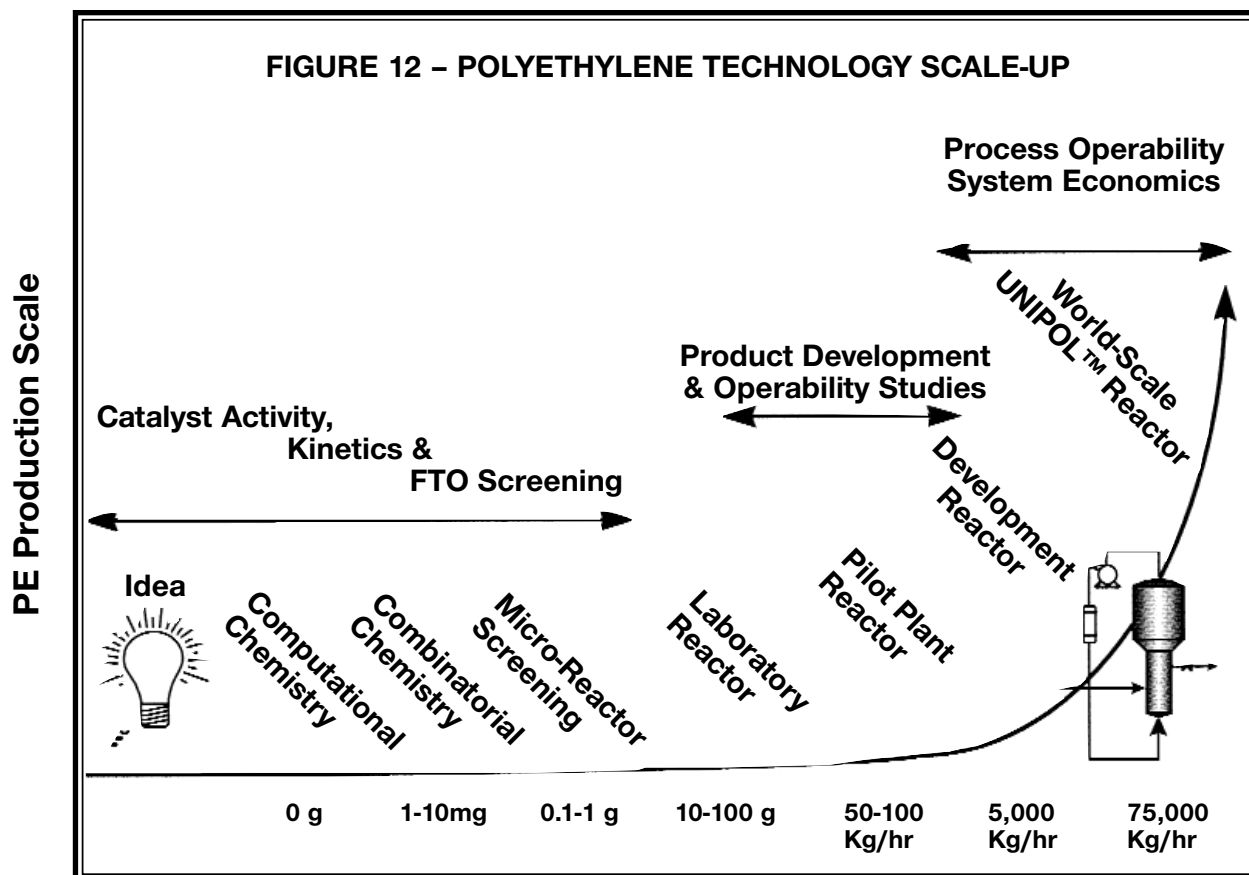
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I would like to elaborate on **Figure 11** to help provide some of the commercial timing perspective we are seeking on the new catalyst chemistries that are emerging from laboratories across our industry. I believe that this figure presents a useful framework for calibrating the timeline associated with commercializing a new catalyst technology, not only for the UNIPOL™ PE Process but also for other polyethylene production processes. With this calibration, we can provide some perspective on where these new developments may reside in the commercialization process and how far away these new catalyst

chemistries may be from meaningfully impacting the polyethylene marketplace. This timeline positioning also provides a sense of what kind of technology investment expense may still lie ahead in the effort to progress these developments fully through the innovation pipeline to reach the “commercial prize.”

Figure 12 scales the technology development steps of **Figure 11** two ways: (1) by assigning resin production rates for each tool with the accompanying heat generation/dissipation requirements and (2) by showing the types of technology challenges addressed with each tool.



In the earliest stages of catalyst research (the catalyst design and performance scoping phase), synthesis, compound characterization, activity evaluation, reaction kinetics mapping, and polymer capability testing define time-consuming tasks that, collectively, pace technology progress and research costs. The laboratory scale of this research keeps costs reasonably contained. In this phase, speed and cost interact, and both depend on the research resources deployed to the effort. The “bench-scale” character of this early stage research work is such that there is limited capability to extrapolate performance scoping data to judge catalyst performance in a commercial PE manufacturing environment.

In the development stages of catalyst technology progression, performance evaluation studies move from lab-scale experiments to pilot

plant campaigns to commercial development reactor trials. This development phase work enables (1) fine-tuning of the catalyst structure and its formulation, (2) large scale testing of prototype products, and (3) process assessment of catalyst responses to important scale factors, such as residence time effects and condensed mode conditions. Other factors include (4) polymer morphology effects on the resin materials handling and (5) process transitioning between polymer grades. This development work also allows the creation of catalyst/reaction models, which will be used to set and control process conditions in larger reactors.

If catalyst development work is executed skillfully, initial technology scale-up to a world-scale commercial reactor will proceed smoothly. Nevertheless, in full-scale reactors, the dynamics of catalyst/process performance can lead to

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operation technology challenges not seen in smaller scale testing. Several commercial trials are sometimes needed to resolve these final issues. In essence, catalyst technology development for world scale UNIPOL™ PE plants is not completed, i.e., considered proven, until several full-scale runs confirm the reliability and process robustness of the technology. Process robustness of a new catalyst technology is a critical performance attribute that is difficult to study anywhere but in the world-scale plant; consequently, it represents one of the most difficult performance features of a new catalyst technology to assess and warrant as proven. Once achieved, startups proceed smoothly and efficiently.

The UNIPOL PE Process has been successfully started up at 42 companies in 82 reactor lines throughout the world. In most of these startups, nameplate production capacity was achieved during the first day or so of operations. This record of success validates the effectiveness of Univation's catalyst discovery and development work processes as well as the operating robustness of the UNIPOL PE Process.

SUMMARY

For the past decade, metallocene catalysis research has been at the forefront in driving technology renewal in the polyolefins industry. As we enter the next decade, mPE supply and demand is now becoming commercially meaningful and showing strong growth.

For the past several years, new ligand-based catalyst technologies have been emerging from various industrial and academic laboratories. These developments illustrate the ever-widening range of catalytic systems for olefin polymerization. The commercial potential of these new chemistries will be determined by the unique benefits they bring relative to incumbent and competing technologies. Many of these new catalysts comprise completely new ligands and even different transition metals. The learning curve is very steep in the early stages of catalyst technology development.

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. And its implementation must not encompass technology encumbered by the patents of others.

In this paper, I have used practical learnings from Univation's experience in developing metallocene catalyst systems for the UNIPOL PE Process as a benchmark for offering commercial perspective on the road ahead for these new emerging chemistries. I believe that the catalyst development pathway challenges described for UNIPOL apply, to some extent, to catalyst development for any world-scale PE manufacturing process

The discovery of a new catalyst chemistry is a very important step but only a first step in a multi-step development journey, which can take many years and involve a tortuous path, sometimes including back-tracking from blind alleys. Like metallocenes, other ligand-based catalyst families encompass an enormous number of potential catalyst structures. Selecting one of these systems to move from research to development to commercial implementation is a critical business decision as the costs to achieve full commercialization can be extremely high.

ACKNOWLEDGEMENT

I would like to acknowledge the significant contributions to the preparation of this paper from my Univation colleagues, Dr. George L. Goeke, Dr. George N. Foster, and Ms. Kathleen A. Sturgeon.



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