

A catalyst for change — a look at olefin polymerization catalysts past, present, and future

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We probably could not imagine life in the 21st century without polymers. Almost everything today can be, and is, made from “plastic”. But this is an inaccurate term, since plastics are only a sub-set of the world of polymers.

The most common polymers are polyolefins, especially polyethylene (better known as Polythene, although this is a trade name owned by DuPont) and polypropylene. However, efficient ways of producing these vital materials are only the result of recent discoveries and have been dependant on the chemistry of catalysts.

Ziegler-Natta catalysts

Since the 1950s, the production of polyolefins has depended on the use of Ziegler-Natta catalysts. These are based on discoveries made by Karl Ziegler and Giulio Natta [1], which were so important that Ziegler and Natta jointly won the Nobel Prize for Chemistry in 1963. However, federal courts have since decided that Robert L Banks and J Paul Hogan were in fact the first to discover these catalysts [2].

Ziegler-Natta catalysts are based on a mixture of a transition metal, commonly a titanium compound, and an alkali metal, most commonly aluminium oxide. Whilst these systems have extremely high activity, their products have variable physical properties. To this day, the systems are little understood, but the monomers (polymer starting materials) react through a number of reaction sites on the catalyst. Unfortunately, this means the polymer can grow from many sites and at different rates, leading to a very wide distribution in the molecular weight, based on the polymer chain length. As the need to control the chain lengths of polymers has grown, the need for a new type of catalyst has also grown. This has given rise to a new breed of catalyst: the metallocene.

The rise of the metallocenes

Modern life has demanded more of the humble polymer. We want polymers that are stronger than steel, lighter than aluminium, and can be dyed any colour imaginable. The Ziegler-Natta system, with its waxy, variable results, could not reliably supply these attributes.

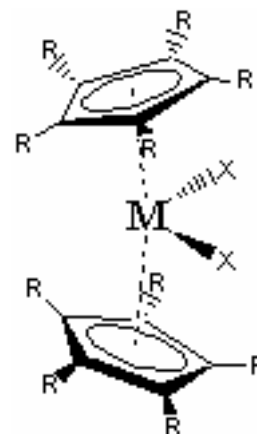


Figure 1: Typical metallocene structure

Metallocene catalysts are, in fact, just as old as the Ziegler-Natta systems [3], but the first systems using them were found to have low activity. It wasn't until 1980, when they were put together with a methyl aluminoxane cocatalyst, that their full potential was realised [4].

Metallocenes are positively charged metal ions, most commonly Titanium or Zirconium, sandwiched between two negatively charged cyclopentadienyl rings (fig 1). Their big advantage over the Ziegler-Natta systems is that they catalyse the reaction of olefins through only one reactive site. Due to this "single site" reaction, the polymerization continues in a far more controllable fashion, leading to polymers with narrow ranges of molecular weight and, more importantly, predictable and desirable properties. Also, it has been found that changing the ligands (functional groups attached to the metal) upon the metallocene molecule can controllably affect the properties of the polymer. This is very attractive to chemical companies trying to keep up with the demand for engineered plastics.

Patenting in the area has been plentiful, with most of the big chemical and oil companies having at least some patents (table 1).

Company	No of patent families
Mitsui Chemicals	446
Exxon Mobil	338
Basell	219
Mitsubishi Chemicals	172
Dow	161
Tosoh	148
Hoechst	135
Sumitomo Chemicals	134
AtoFinaElf	128
Phillips	115

Table 1: Top 10 companies patenting metallocenes from 1994-2003

The patenting of new metallocene catalysts hit a peak in 1999, with 295 new metallocenes out of a total of 572 new catalysts for polyolefins [5]. Since that time, the number of new metallocenes has fallen. But so has the total number of new catalyst inventions, probably reflecting the downturn in the chemical industry during that time.

What is more significant is that the share of metallocenes of all novel polymerization catalysts that have been patented has fallen in recent years – from a peak of 55% of all new patents families in 1997 to 42% in 2003 (fig 2).

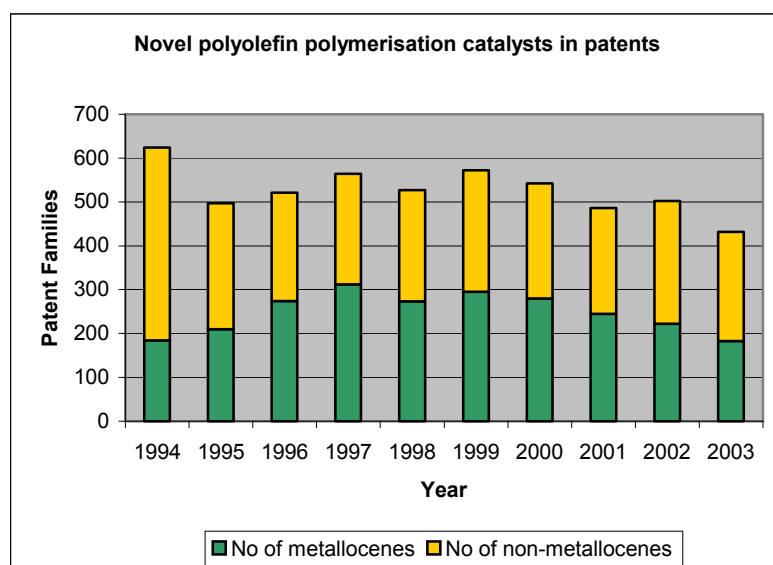


Figure 2: ratio of new metallocene catalysts

The drawback of metallocene catalysts is that they are unable to polymerize polar molecules, such as common acrylics or vinyl chloride. This is due to the metallocenes' oxophilicity – their propensity for binding to oxygen. Introduction of a polar monomer into a reaction system will kill the catalyst activity to almost zero. So polymer chemists have started searching for new types of single site catalysts.

Post-metallocenes

A lot of research is now being directed at other types of chemical that can produce polyolefins with the desired properties. Currently, work has progressed using metals from all over the Periodic Table. But one area in particular is proving advantageous: late transition metal compounds.

Late transition metal compounds

Catalysts using late transition metals – those metals from groups 6 and higher in the Periodic Table – have become increasingly utilized. These compounds have good polymerization activity, although slightly less than metallocenes. However, crucially they can polymerize reactions with polar monomers. The most commercially advanced of this type of catalysts are the Brookhart catalysts [6], which are diimine complexes of palladium or nickel (fig 3).

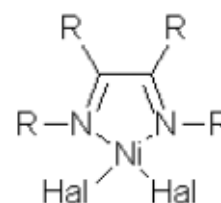


Figure 3: Typical structure of Brookhart catalysts

Patenting of late transition metal catalysts has been increasing over the last 10 years, although again with a slight decrease along with all catalyst patenting since 2000 [7].

What is interesting here is that the share of late transition metal compounds of all novel polymerization catalysts that have been patented has significantly risen – from 21% of all new patents families in 1994 to 42% in 2003 (fig 4).

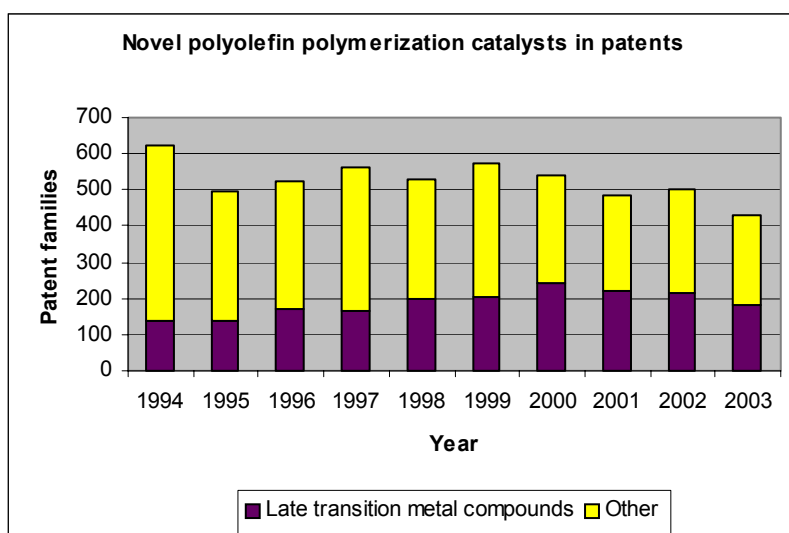


Figure 4: Ratio of all new late transition metal compound catalysts

We also can see a change in the top patenting companies (table 2), with Exxon Mobil and Mitsui Petrochemicals relinquishing their tight hold on the metallocenes market.

Conclusion

Although it is a little early to be sounding the death knell of the metallocene catalyst, it would seem that the next generation of olefin polymerization catalysts are likely to be late transition metal catalysts.

Company	Number of patent families
Mitsui Chemicals	167
BASF	119
Mitsubishi Chemicals	115
Phillips Petroleum	110
Basell	94
BP	88
Nippon Zeon	80
Tosoh	68
Exxon Mobil	67
Shell	50

Table 2: Top 10 companies patenting late transition metal catalysts from 1994-2003

References

- [1] Patent US 2,691,647 (12 October 1954) – Conversion of ethylene and/or propylene to solid polymers in the presence of group 6a metal oxides and alkali metals.
- [2] Patent US 2,642,467 (16 June 1953) – Production of high-octane fuel components
- [3] Patent US 2,827,446 (18 March 1958) – Polymerization of ethylene
- [4] Patent DE3007725 (1980) – Verfahren zur Herstellung von Polyethylen, Polypropylen und Copolymeren
- [5] Source data – *Derwent World Patents Index*[®]
- [6] Patent WO 96/23010 (01 August 1996) – Alpha-olefins and olefin polymers and processes therefore
- [7] Source data – *Derwent World Patents Index*