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From the Lab Bench to the Plant: How to Commercialize a Metallocene Catalyst?

Helmut G. Alt

Laboratorium für Anorganische Chemie, Universität Bayreuth, D-95440 Bayreuth, Germany
e-mail: helmut.alt@uni-bayreuth.de

SUMMARY: In order to apply metallocene catalysts for the polymerization of ethylene in the commercial "slurry loop process" it is necessary to heterogenize the homogeneous catalysts and to produce resins with attractive properties. A solution to these problems is the self-immobilization of ω-alkenyl functionalized catalysts that can produce polyethylenes with evenly distributed ethyl branches in the polymer chain without a comonomer. The new resin is produced at Chevron Phillips Company, USA, and has the trade name mPact.

Introduction

Metallocene catalysts opened the door to a new class of olefin polymerization catalysts.[1-4] They have excellent activities and they are able to produce new materials with new properties.[5] However, the challenge to use such catalysts for commercial processes is connected with a series of conditions they must fulfill:

- They must have high activities in order to compensate eventual higher synthesis costs compared with other competitive catalysts on the market.
- For the commercial slurry loop process the originally homogeneous catalysts must be heterogenized.
- They must be able to produce new materials with better properties than the established resins.

We found a solution for all these problems.

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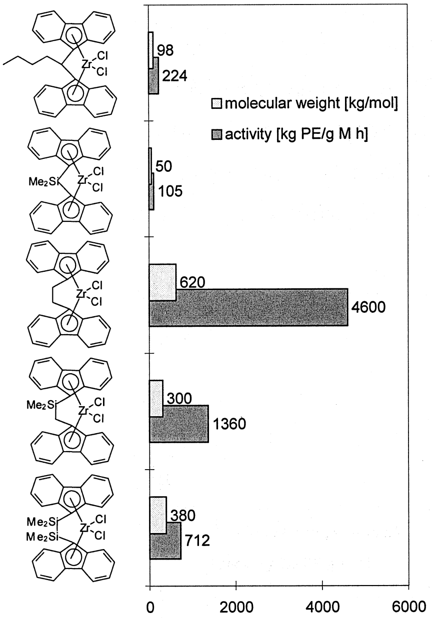
Results and Discussion

1. Metallocene catalysts with high activities

In the series of various ansa cyclopentadienyl, indenyl and fluorenyl derivatives of metallocene complexes, the fluorenyl complexes show the highest activities as homogeneous ethylene polymerization catalysts.[6)] The reason seems to be the ring slippage behavior of fluorenyl ligands that can provide additional coordination sites during the course of the polymerization.

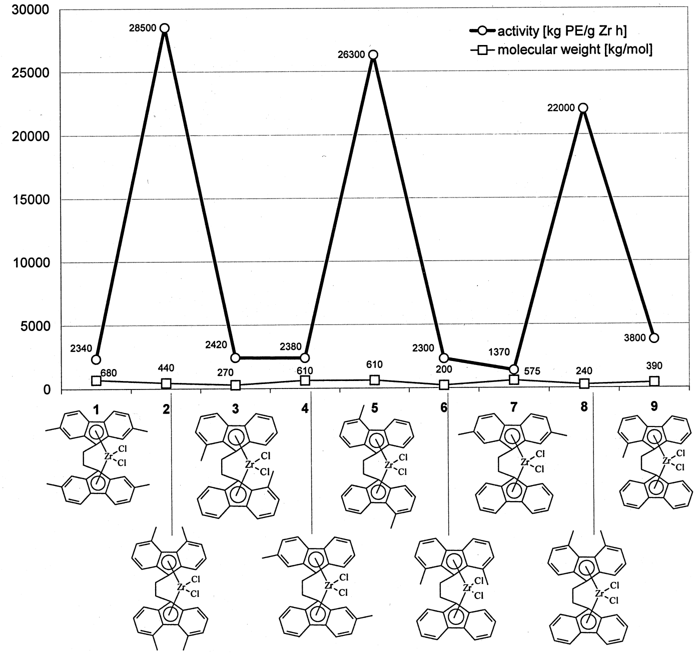
In the series of *ansa* metallocene complexes the C_2 bridged bis(fluorenyl) derivatives have the highest activities for ethylene polymerization.[7-9)]



Polymerization conditions: Tp = 60°C; MAO, Al/Zr = 20000; solvent n-pentane; 10.0 bar pressure

Fig. 1: Polymerization of ethylene with various ansa bis(fluorenyl) complexes

In the case of methyl substituted derivatives the position of the substituents determines the activity.[8)]



Polymerization conditions: T_p=60°C; MAO, Al/Zr=20000, solvent: n-pentane, 10.0 bar ethylene pressure.

Fig. 2: Influence of the position of methyl substituents in complexes of the type (Flu′-C_2H_4-Flu′)$ZrCl_2$ (Flu′ = substituted fluorenyl) on the catalyst activities and the molecular weights of the produced polyethylenes

Positions 4 and 5 are the best for substitution. Obviously, substituents in these positions have some sort of a spacer effect for the bulky MAO counter anion that is formed in the catalyst activation process.[10)]

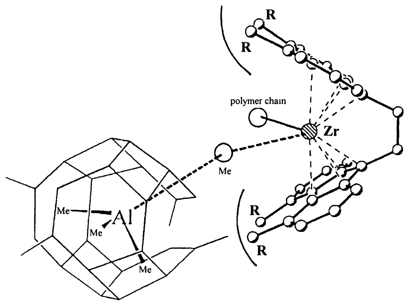
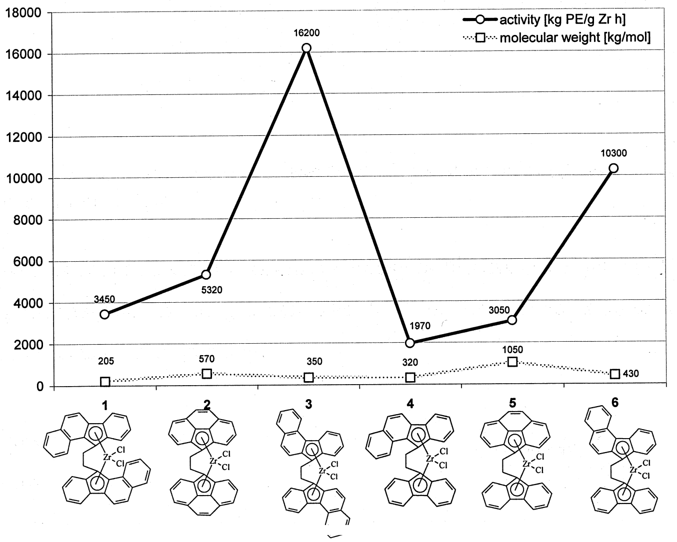


Fig 3: Influence of methyl substituents in the 4 and 5 positions of the fluorenyl ligand on the polymerization activity

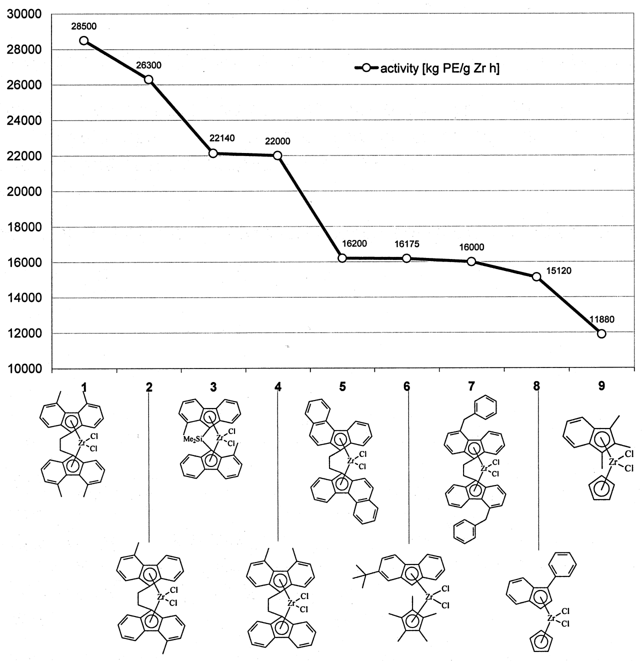
The other positions could be disadvantageous because of hindered orientation of the polymer chain during the polymerization process. The same positive effect can be achieved by anellated ring systems in these positions.



Polymerization conditions: T_p=60°C; MAO, Al/Zr=20000, solvent: n-pentane, 10.0 bar ethylene pressure.

Fig 4: Influence of fused ring systems in complexes of the type (Flu'-C_2H_4-Flu')$ZrCl_2$ (Flu′ = fluorenyl ligand with an anellated ring) on the catalyst activities and the molecular weights of the produced polyethylenes

It is interesting to note that out of 700 metallocene complexes synthesized in my research group, the five most active catalysts belong to the family of ansa bis(fluorenyl) complexes.[8)]



Polymerization conditions: T_p=60°C (**1**,**2**,**4**,**5**,**7**,**9**), 30°C (**3**,**8**), 10°C (**6**); MAO; Al/Zr=20000 (**1**,**2**,**4**,**5**,**7**), 8000 (**3**), 1000 (**6**, **8**, **9**), in pentane.

Fig. 5: Top 9 of our most active metallocene complexes for ethylene polymerization

2. The heterogenization of homogeneous catalysts

One reason for the high activity of metallocene complexes is their homogeneous nature. In solution every single molecule has the potential to act as a catalyst (single site catalyst) for the application in the slurry loop process. However, the catalyst must be heterogeneous in order to avoid "fouling" of the reactor: the formed polymer sticks on the reactor walls and prevents an efficient temperature control during the polymerization process.

One approach to avoid fouling is to fix the homogeneous catalyst on a support like silica or functionalized polystyrene [11-13]. An example illustrates how this can be achieved.

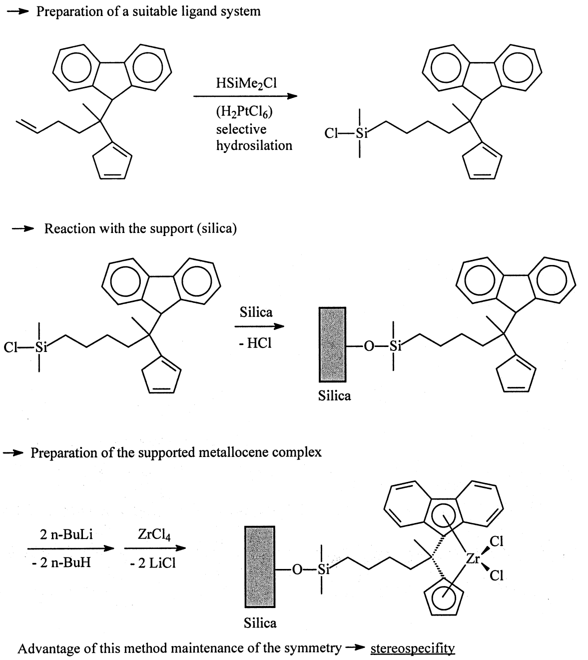


Fig. 6: Silica as support for the synthesis of a heterogeneous metallocene catalyst precursor

This synthetic procedure is cumbersome and allows the immobilization of only one catalyst at a time.

The problem can be solved in a very elegant manner by the design of complexes that are catalysts and olefin or alkyne at the same time:

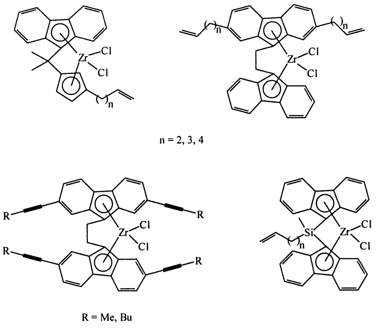


Fig. 7: Functionalized catalyst precursors with an olefin or alkyne group

Such compounds can be activated with MAO in solution and then form a heterogeneous catalyst. As soon as ethylene is bubbled through the solution a precipitate is formed that adopts the color of the solution. The supernatant liquid is colorless and clear.[14-16)]

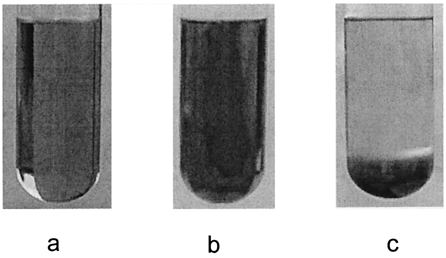


Fig. 8: Self-immobilization of a metallocene catalyst

(a = homogeneous solution of the catalyst precursor in toluene,
b = homogeneous solution of the activated catalyst in toluene.
c = self-immobilized catalyst obtained from prepolymerization with ethylene)

We assume that the originally homogeneous catalyst polymerizes ethylene and copolymerizes other catalysts simultaneously. As a result a heterogeneous network is formed.

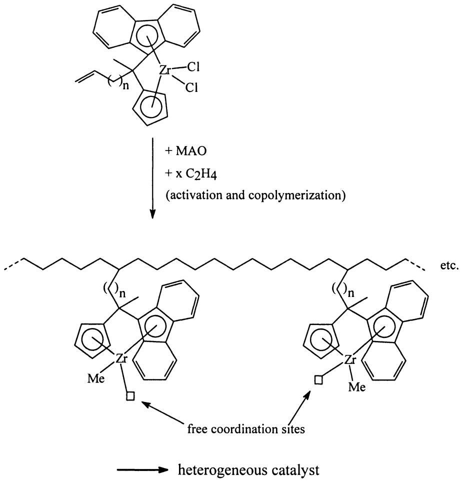


Fig. 9: Proposed mechanism for the "self-immobilization" of a homogeneous metallocene catalyst

The extent of copolymerization can be controlled with the amount of ethylene in the prepolymerization step.

The activity of such self-immobilizing catalysts and the molecular weight of the produced polyethylene depend on the length of the ω-alkenyl substituent and its position in the ligand system.[16)]

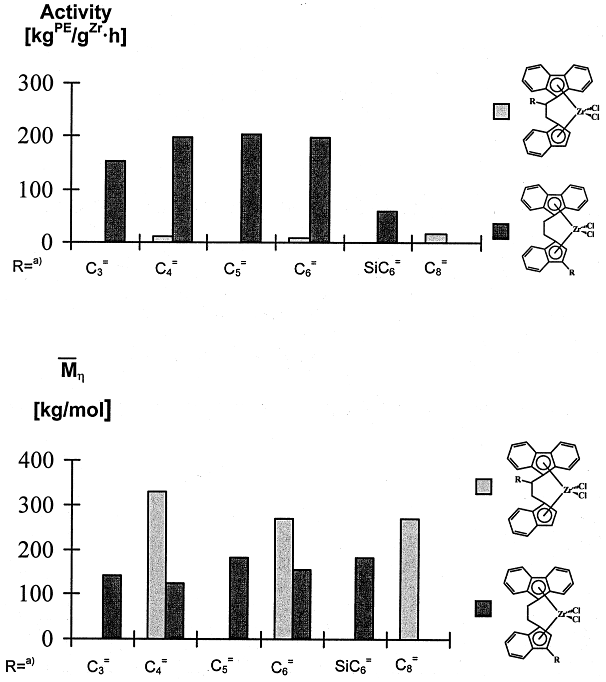


Fig. 10: Influence of the position and the chain length of the ω-alkenyl substituent on the activity of the catalyst and the molecular weight of the produced polyethylene. Polymerization conditions: 60 °C, pentane, 10 bar ethylene pressure, MAO (Al : Zr = 3000 : 1), 1 hour

For instance, substitution in position 3 of a C_2 – bridged cyclopentadienylidene fluorenylidene complex is much better for high activities than substitution in the bridge.

Just recently we found that also metallacyclic metallocene compounds are suitable candidates for this new support technique combining the advantages of homogeneous and heterogeneous catalysis.[17)]

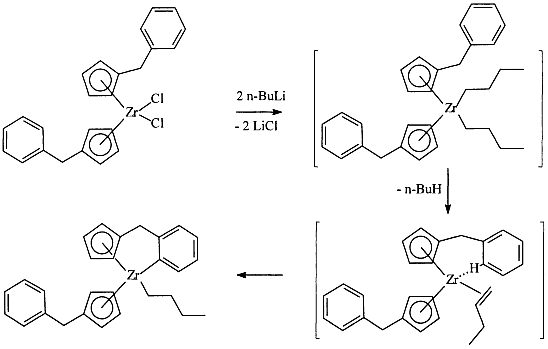


Fig. 11: Synthesis of metallacyclic metallocene complexes

In addition to high activity the metallacycles are completely halogen free and the produced polyethylene can be thermally recycled without causing any corrosion or environmental problems.

3. New materials

The production of new materials is the hardest part of the enterprise because the results cannot be predicted or planned. We were lucky. Chemists from Phillips Petroleum Company, USA, found that the polyethylene that was produced with some of these self-immobilizing catalysts had excellent properties due to ethyl branching that occurred during polymerization. The ethyl branches were evenly distributed along the hydrocarbon backbone. They are formed from the monomer and their extent of formation does not depend on the reaction conditions but on the nature of the corresponding catalyst. In addition these complexes allowed copolymerization with other olefins.

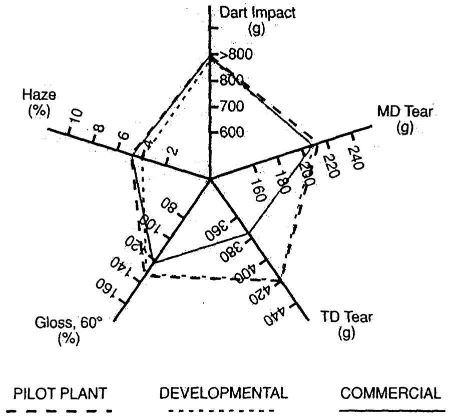


Fig. 12: Film properties of m-LLDPE produced in different reactors

We still do not have a satisfying explanation how these regular ethyl branches are formed without any comonomers. This is another argument for the statement: metallocene catalysts can be unpredictable.

This new material is called mPact and it is able to form very transparent films. Indeed, mPact is one of the best materials on the market in this respect.

Acknowledgement

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