

*DPI Annual Meeting 2007*

**Adventures in catalytic olefin polymerization**  
- or -  
**Brave deeds of molecule-tamers**

*Vincenzo Busico, DPI SC Polyolefins  
Federico II University of Naples (Italy)*



## Summary

- **[Excusatio non petita]** Why insisting with polyolefins ?
- **[Simple] Answer #1:** Because we don't know enough about polyolefins
- **Answer #2:** Because we don't know enough about organometallic catalysis, and studying catalytic olefin polymerization is the easiest way to learn more
- **Answer #3:** Because we must produce talents for the booming polyolefin industry worldwide
- **Answer #4:** Because we can invent lots of new stuff and make more money
- **[Personal] Answer #5:** Because I like it and have fun



To begin ...

... a few slides of propaganda



## The Nobel Prize in Chemistry 2001

"for their work on chirally catalysed hydrogenation reactions"

"for his work on chirally catalysed oxidation reactions"



**William S. Knowles**

St. Louis, MO, USA

b. 1917



**Ryoji Noyori**

Nagoya University  
Nagoya, Japan

b. 1938

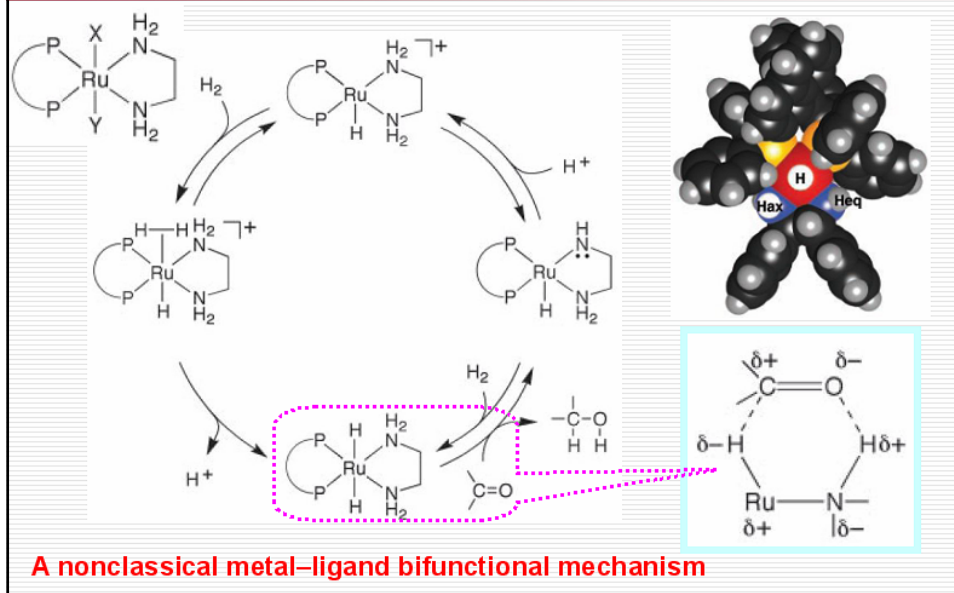


**K. Barry Sharpless**

The Scripps Research  
Institute  
La Jolla, CA, USA

b. 1941

## Asymmetric hydrogenation of simple ketones by BINAP/diamine–ruthenium complexes



## Significance of BINAP Chemistry

- ✚ Excellent enantioselectivity (90-100 % ee).
- ✚ Wide scope of substrates (C=O, C=C, C=N).
- ✚ Rivals or exceeds enzymes: e.g. 2,400,000 (TON), 228,000 h<sup>-1</sup>, 63 S<sup>-1</sup> (TOF).
- ✚ Development of pharmaceuticals and synthetic intermediates.
- ✚ Successful industrial applications.
- ✚ An enormous scientific or technological impact and even more general social benefits.

## Comparative propaganda

### Significance of BINAP Chemistry

- ✦ Excellent enantioselectivity (90-100 % ee).
- ✦ Wide scope of substrates (C=O, C=C, C=N).
- ✦ Rivals or exceeds enzymes: e.g. 2,400,000 (TON), 228,000 h<sup>-1</sup>, 63 S<sup>-1</sup> (TOF).
- ✦ Development of pharmaceuticals and synthetic intermediates.
- ✦ Successful industrial applications.
- ✦ An enormous scientific or technological impact and even more general social benefits.

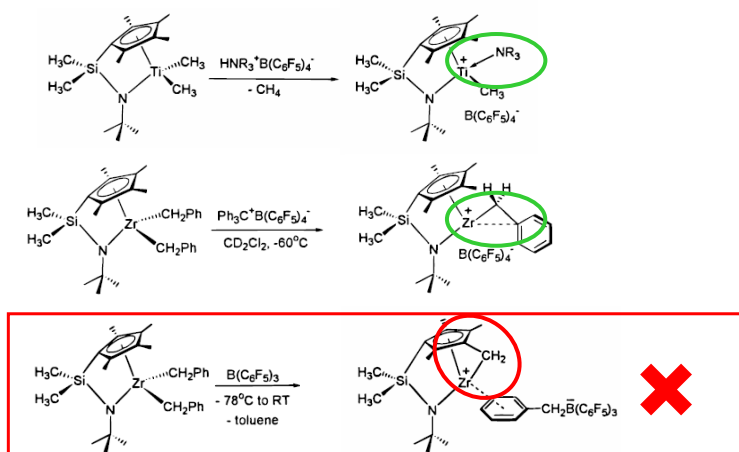
### Significance of ZN Chemistry

- Astonishing enantioselectivity (>99.8% e.e.)
- Routs enzymes: e.g. 100,000,000 (TON), 36,000,000 h<sup>-1</sup>, 10,000 s<sup>-1</sup> (TOF)
- Development of PP's, PE's, (thermoplastic) elastomers
- Outrageously successful industrial applications
- Has changed the world

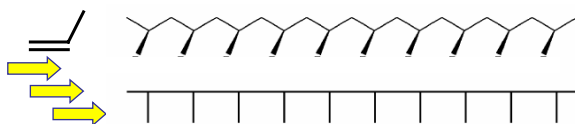


## The first step: pre-catalyst activation

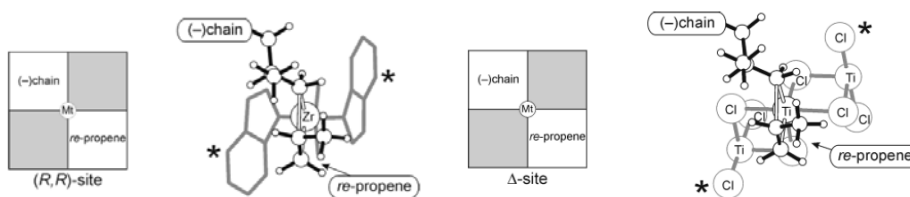
(Read: changing a well-behaved molecule into a beast)



## Molecular control in propene polymerization (Taming the beast – Exercise 1: Enantioselectivity)



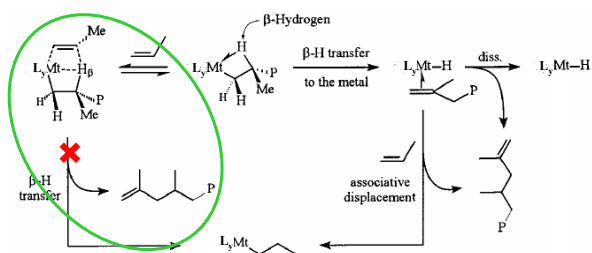
In some cases, **ideal regio- and stereostructure** (chain ends detectable, defects undetectable in  $^{13}\text{C}$  NMR spectra !!!)



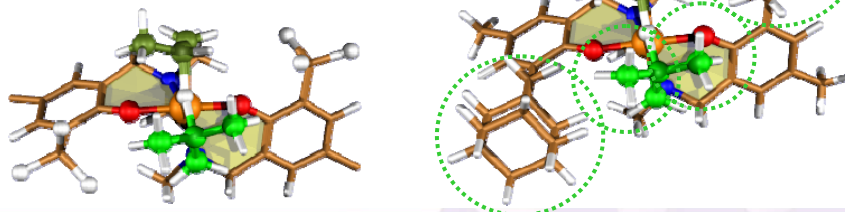
Ref.: Corradini, P. et al. *Acc. Chem. Res.* **2004**, 37, 231-241



## Molecular control in propene polymerization (ctd) (Taming the beast – Exercise 2: Propensity to chain transfer)



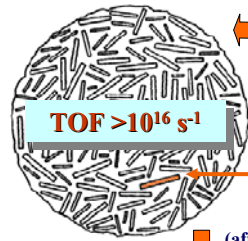
**Living catalyst !**



Ref.: Busico, V. et al. *Macromolecules* **2004**, 37, 8201-8203



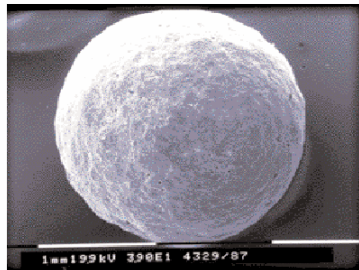
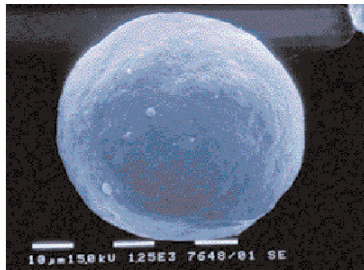
## Morphology control in propene polymerization (... and now, ladies and gentlemen, trillions of beasts together !)



Secondary particle of  $\text{MgCl}_2$   
( $100\ \mu\text{m}\ \varnothing$ ,  $\sim 1\ \mu\text{g}$ ,  $\sim 10^{12}$  primary particles)

Primary particle of  $\text{MgCl}_2$   
( $< 10\ \text{nm}\ \varnothing$ ,  $\sim 1 \times 10^{-18}\ \text{g}$ )

(after pre-polymerization)



➔ Polymer granule ( $> 1\ \text{mm}\ \varnothing$ )

## After the propaganda ...

... the hard reality

## We understand a catalyst when we know...

- ... the structure(s) of the active species (including counterion and solvent effects when that is the case)
- ... their concentration
- ... the full molecular kinetics of the reaction
- ... the effect(s) of the main physical and chemical reaction variables
- ... the **true** TON and TOF

*When the above holds, rational catalyst design is / should be possible  
To the best of my knowledge, the above does not hold for any olefin polymerization catalyst so far, and I doubt that it can be claimed for any organometallic catalyst*



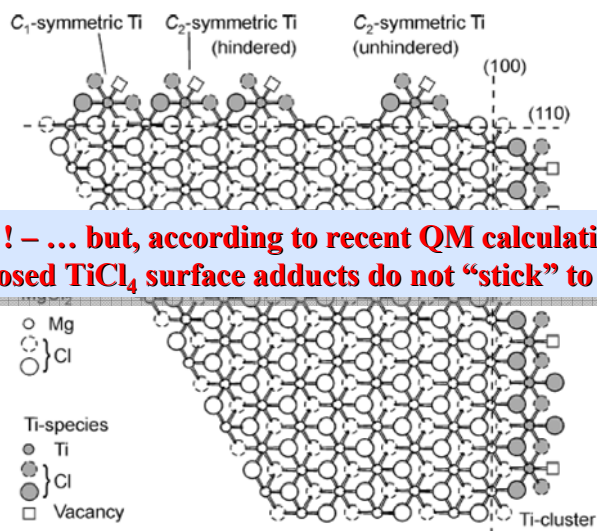
## Where do we stand with olefin polymerization catalysts ?

Level of understanding: ✘ = Unsatisfactory; + = Fair; ✓ = Satisfactory

- ✘ Absolute and relative catalytic activities
- + Chemo-, ✓ regio-, ✓ enantio-, + stereoselectivity
- + Molecular mass capability
- + Chain transfer pathways
- + De-activation pathways
- + Possible formation of “dormant” states
- ✘ Propensity to [reversible] trans-alkylation

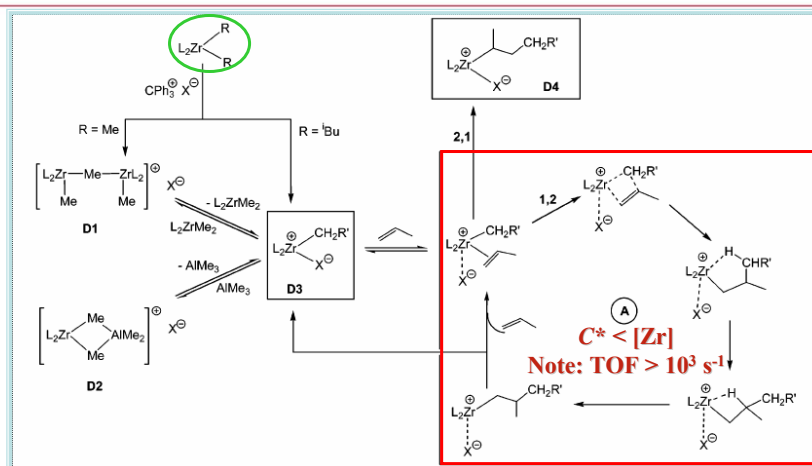


## An extreme case of fundamental ignorance High-yield $\text{MgCl}_2$ -supported Ti-based catalysts for iPP



**Nice! – ... but, according to recent QM calculations, most proposed  $\text{TiCl}_4$  surface adducts do not “stick” to  $\text{MgCl}_2$  !!!**

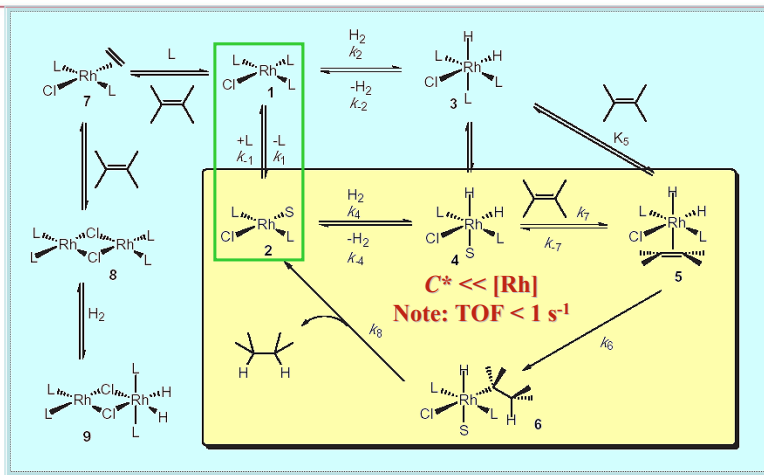
## A tentative mechanistic scheme for catalytic olefin polymerization in homogeneous phase



Bochmann, M. et al. JACS 2003, 125, 7641



## A similar case in catalytic olefin hydrogenation



Halpern, J. et al. *J. Mol. Cat.* **1976**, 2, 65; *JACS* **1977**, 99, 8055; *JACS* **1980**, 102, 838; *Science* **1982**, 217, 401



## How can we understand more?

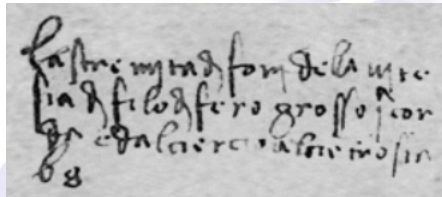
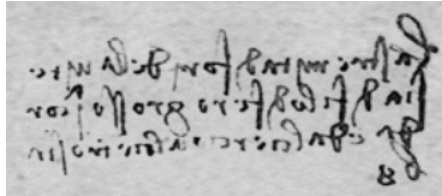
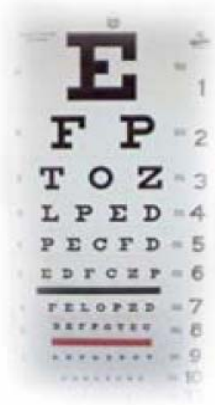
### The unique advantage of polymerization reactions

- **Polymer chains are ideal systems to store and transport information** (just think about DNA and RNA)
- In particular, a **synthetic polymer chain is a permanent record of the statistical chain of events which constituted the polymerization process.** The complete story of the reaction is written in there. This represents an extraordinary advantage for mechanistic studies
- Of course, in order to **read the message**, one or more techniques are needed for the determination of chain microstructure. For vinyl polymers, **<sup>13</sup>C NMR** is the elective tool



There is reading ...

... and reading

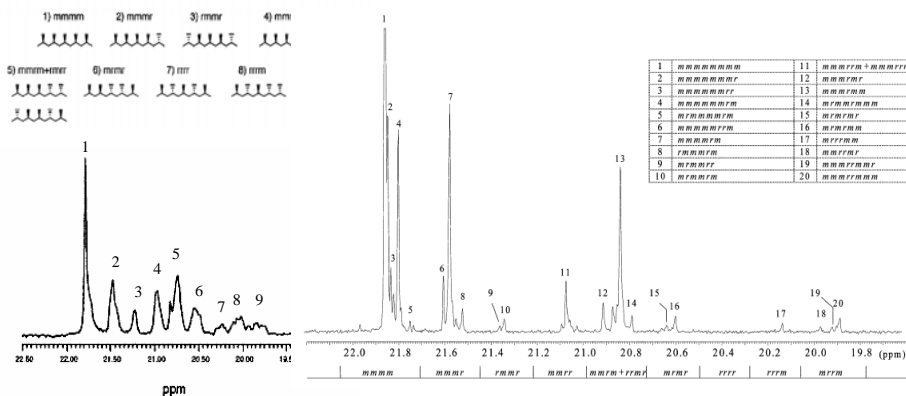


## Reading [decoding] a polyolefin chain

There is reading ... and reading

From pentads ...

... to heptads/nonads

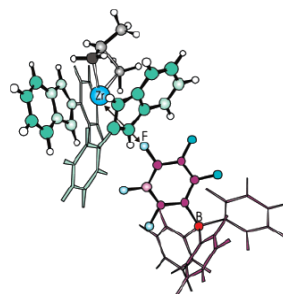
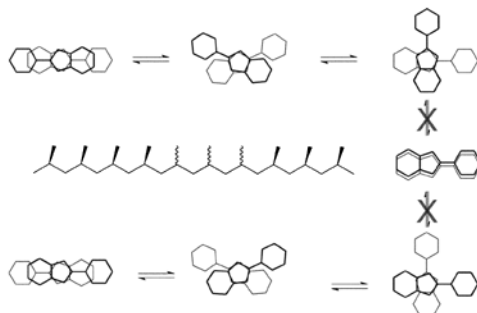
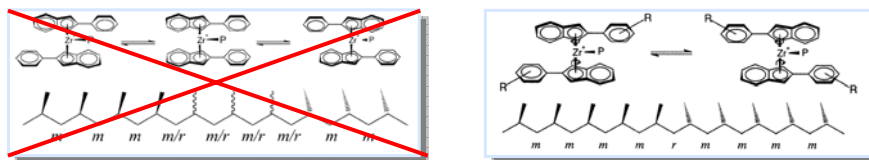


Full assignment of the 150 MHz  $^{13}\text{C}$  NMR spectrum of PP :  
Segre, A.; Busico, V. et al. *Macromolecules* **1997**, *30*, 6251



## Writing in a polyolefin chain, 1

### Stereoblock polypropylenes made with “oscillating” metallocenes



Coates, G. W.; Waymouth, R. M. *Science* **1995**, 267, 217-219  
 Busico, V. et al. *J. Am. Chem. Soc.* **2003**, 125, 5451-5460

Project #102  

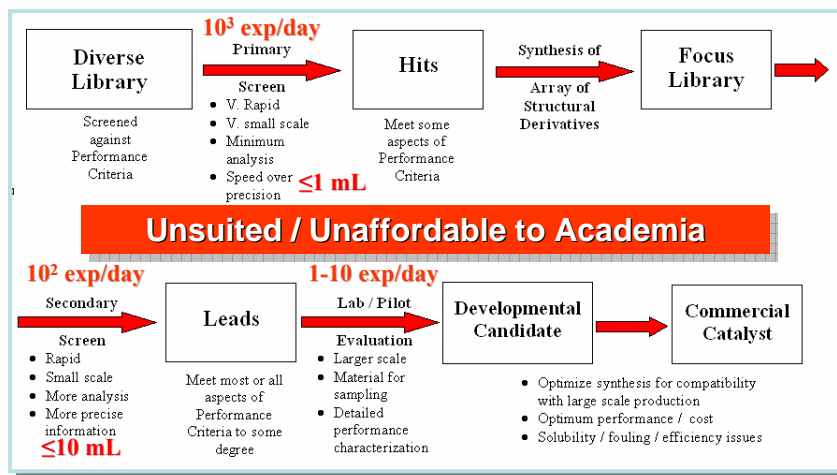

## Towards a better understanding of olefin polymerization catalysts: the DPI strategy \*

- Identification of a suitable number of convenient basic precatalyst structures
- **Parallel** structural amplification of the above
- **High throughput** homo- and copolymerization studies under multiple activation conditions, with **full microstructural polymer analysis**
- Active site counts
- Solution NMR studies of catalytic species and ion pairs
- Ex-post and possibly predictive **high throughput** computational modeling

\* Projects #633, 635, 639, 641, 644/5



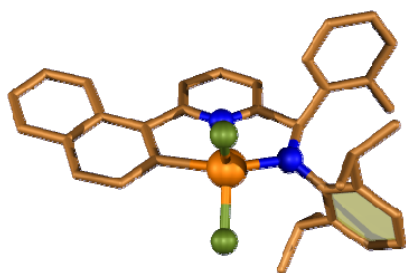
## High Throughput Experimentation in olefin polymerization How to discover new catalysts \*



\* Thanks to Dr. J.C. Stevens, The Dow Chemical Co.



## High Throughput Experimentation in olefin polymerization How to discover new catalysts (ctd)



**Versify™ Platform  
(Dow Chemical)**

### New (pyridylamide)Hf catalysts

- Nonconventional structure
- Highly active
- Thermally robust
- Highly isotactic-selective for PP
- Good co-monomer incorporation in ethene/1-alkene copolymerizations
- Exceptionally high polymer molecular mass capability

(a) Frazier, K. A.; Boone, H. W.; Vosejka, P. C.; Stevens, J. C. U.S. Patent 6,953,764.  
 (b) Bousie, T. R.; Diamond, G. M.; Goh, C.; Hall, K. A.; LaPointe, A. M.; Leclerc, M. K.;  
 Murphy, V.; Shoemaker, J. A. W.; Turner, H.; Rosen, R. K.; Stevens, J. C.; Alfano,  
 F.; Busico, V.; Cipullo, R.; Talarico, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 3278-3283.



## High Throughput Experimentation in olefin polymerization How to screen & tune catalysts

- **Primary Screening by HTC [DPI #641]**

Tuning of [known] ligand frameworks  
by means of in-silico structural amplification



- **Parallel Synthesis of "Hits" [DPI #633]**



- **Secondary Screening by HTE [DPI #644/5]**

Thorough catalyst testing in mini-reactors under  
multiple activation conditions



**Suited / Affordable to Academia**



## High throughput catalyst screening & tuning workflow at U-Naples

- HTC Primary Screening**  
Opteron & HP ES45 Clusters



Inst. Q1/2008

- Parallel Synthesis of "Hits"**  
Symyx Core Module

**Off-Line Integrated Analytical Toolkit**  
GC-MS, TLC, ...



- HTE Secondary Screening**  
Symyx PPR24®

**Off-Line Integrated Analytical Toolkit**  
Bohdan WS,  $^1\text{H}/^{13}\text{C}$  NMR, HT-GPC



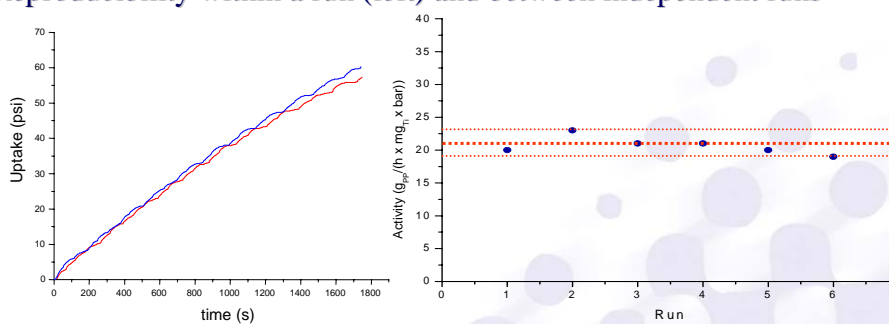
## The secondary screening platform at U-Naples Symyx PPR24<sup>®</sup> Olefin Polymerization Workflow



## The secondary screening platform at U-Naples Propene polymerization with a HY-ZNC



Reproducibility within a run (left) and between independent runs



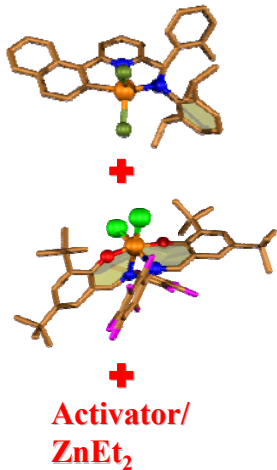
### Experimental conditions:

$T_p = 70^\circ\text{C}$ ;  $p(\text{C}_3\text{H}_6) = 3.4 \text{ bar}$ ;  $p(\text{H}_2) = 0.4 \text{ bar}$ ; heptane solvent, 5 mL;  
solid catalyst, 0.20 mg [0.092  $\mu\text{mol}(\text{Ti})$ ];  $[\text{TEAL}]/[\text{Ti}] = 170$ ; cutoff yield, 100 mg(PP)

Project #644/5



## Writing in a polyolefin chain, 2 Block copolymerization via “chain shuttling”



Good 1-octene incorporation in  
C<sub>2</sub>=/C<sub>8</sub>= copolymerization  
[noncrystallizable/“soft” copolymer]

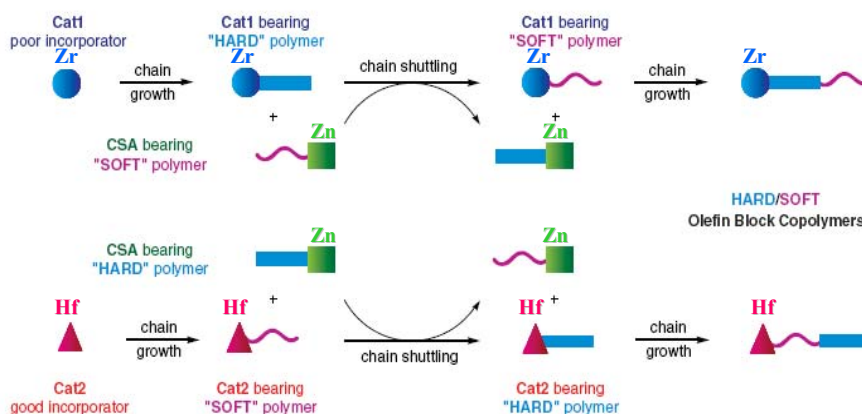
Poor 1-octene incorporation in  
C<sub>2</sub>=/C<sub>8</sub>= copolymerization  
[crystallizable/“hard” copolymer]

→ **Hard/Soft Block Copolymers**  
via fast and reversible trans-alkylation

Arriola, D. J.; Carnahan, E. M.; Hustad, P. D; Kuhlman, R. L.;  
Wenzel, T. T. *Science* **2006**, 312, 714-719



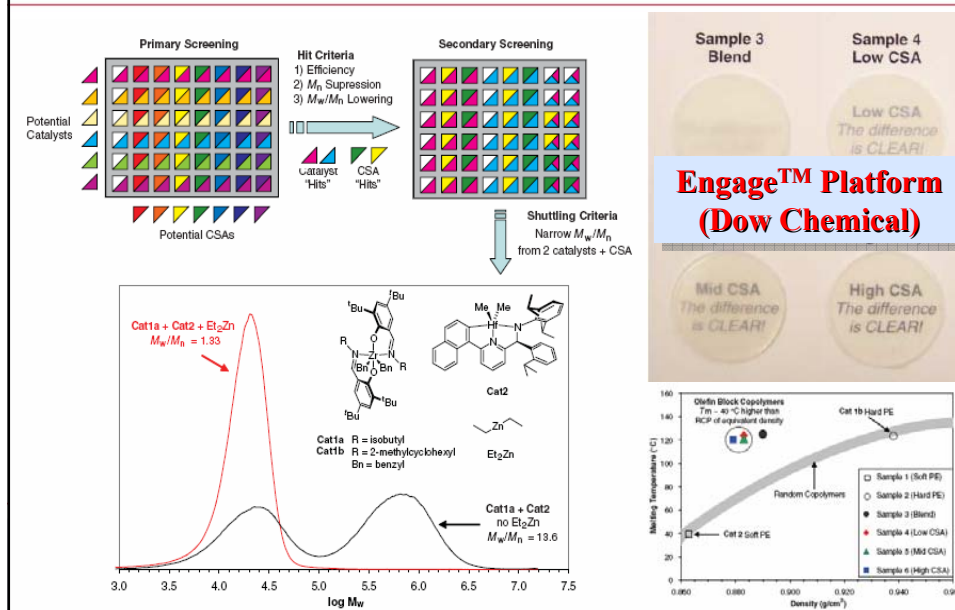
## Writing in a polyolefin chain, 2 Block copolymerization via “chain shuttling” (ctd)



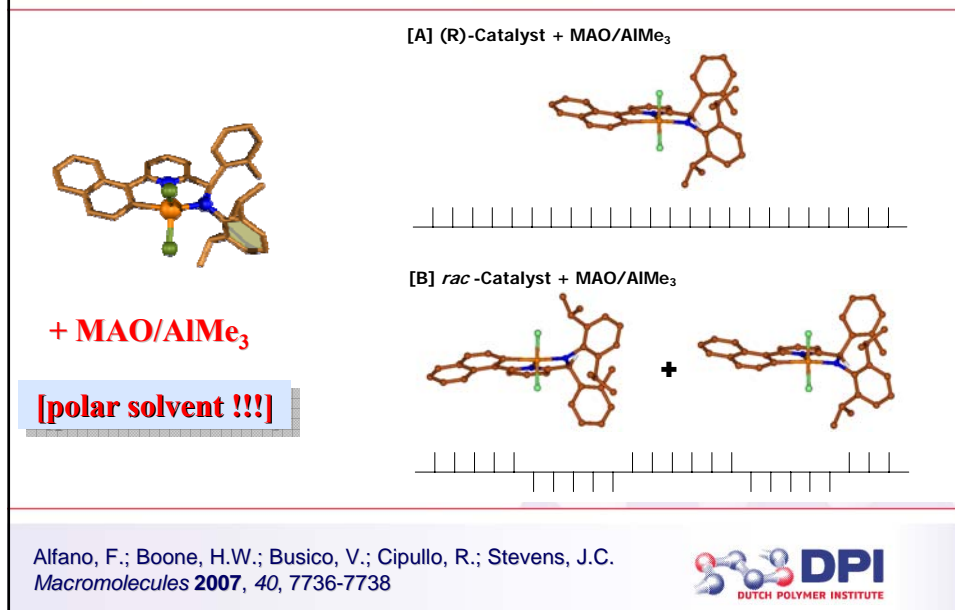
Arriola, D. J.; Carnahan, E. M.; Hustad, P. D; Kuhlman, R. L.;  
Wenzel, T. T. *Science* **2006**, 312, 714-719



## Writing in a polyolefin chain, 2 Block copolymerization via “chain shuttling” (ctd)



## Writing in a polyolefin chain, 3 Stereoblock propene polymerization via “chain shuttling”





## Concluding remarks

- Now you know why we insist with polyolefins
- Now you realize that there is still much to understand about polyolefins
- Now you see how much (in catalysis, processes and materials) is still left for innovation in polyolefins
- Do you blame me for liking polyolefins and having fun with them ?