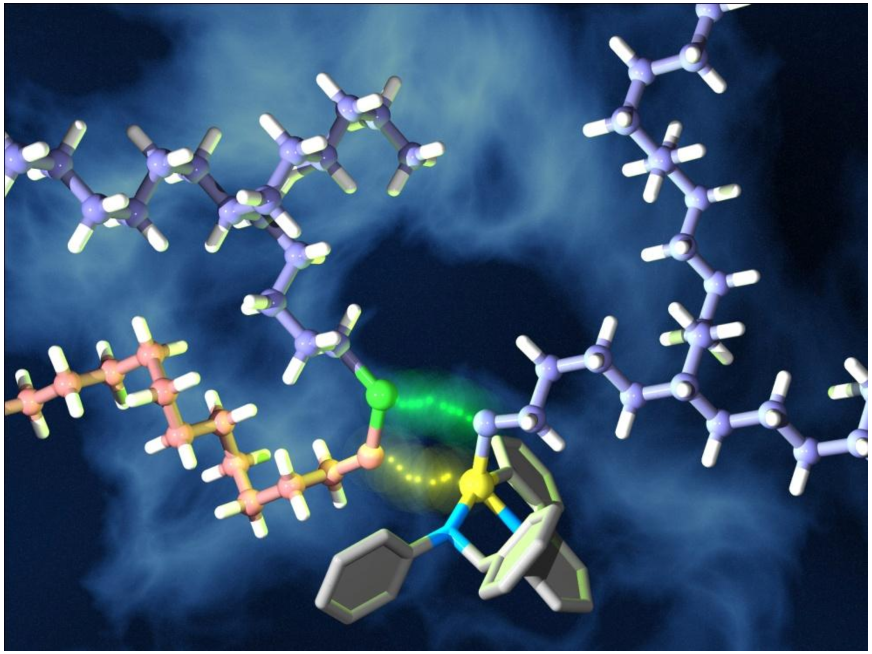
Performance Polyolefins by Molecular Design

Edmund (Ted) Carnahan
Fellow, Performance Plastics R&D
The Dow Chemical Company

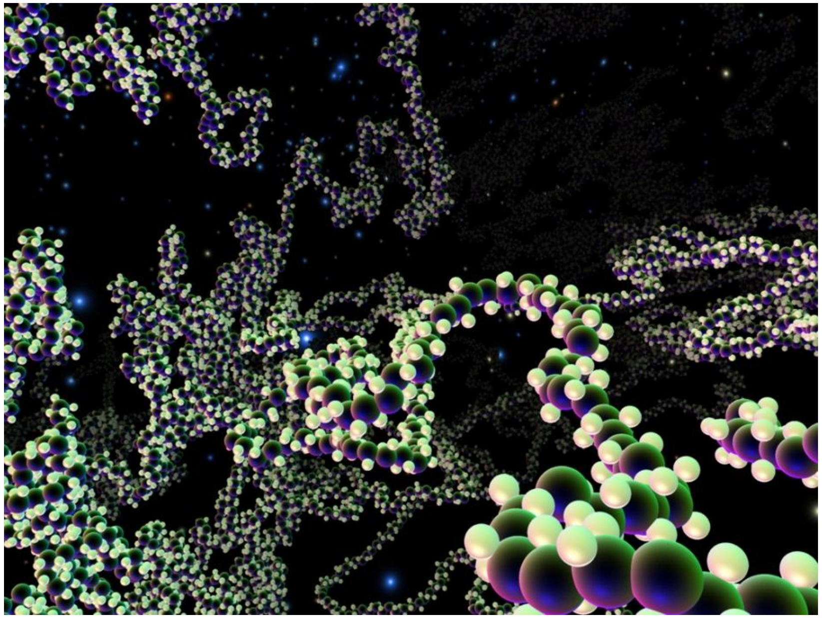


Advances in Polyolefins 2011

Why Continue to Study Polyolefin Catalysis?

"[W]hen I happen to declare that I keep on studying enthusiastically Ziegler-Natta chemistry, the majority of my colleagues look at me as at an elderly and somehow pathetic gentleman who refuses to admit that the object of his juvenile passion is now withered."

Vincenzo Busico, *Macromol. Chem. Phys.* **2007**, *208, 26.*



http://www.molecularium.com/

Customers Like Olefin Solutions

- Polyolefin plastics are inexpensive, non-toxic, light weight, recyclable, and easy to process.
- If an olefin solution meets performance needs, it is usually used.

DOW

Polyolefins are Everywhere

- Global annual demand exceeds 120 million metric tons (>2.8 x 10^{11} lbs)!
- Growing at ~5% per year, faster growth in emerging economies

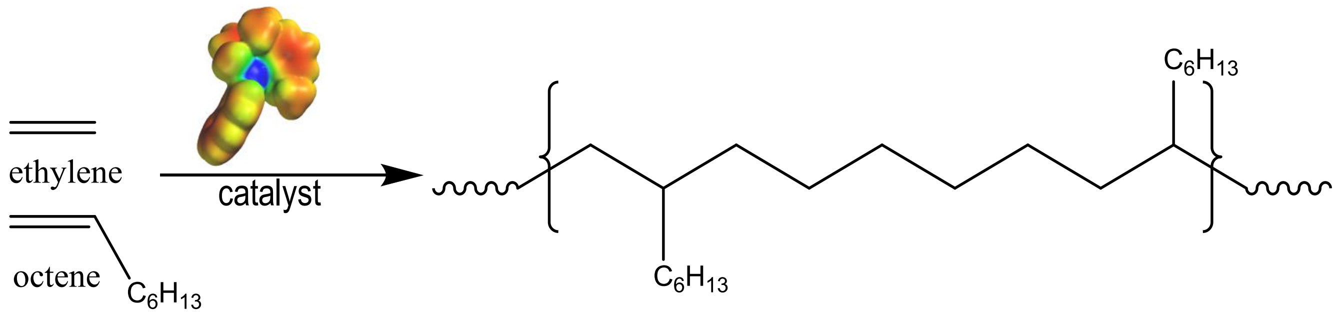


Consumer Durables and Appliances
Electrical and Electronics
Food and Specialty Packaging
Health and Hygiene
Industrial and Consumer Packaging
Pipes and Fittings
Rigid Packaging

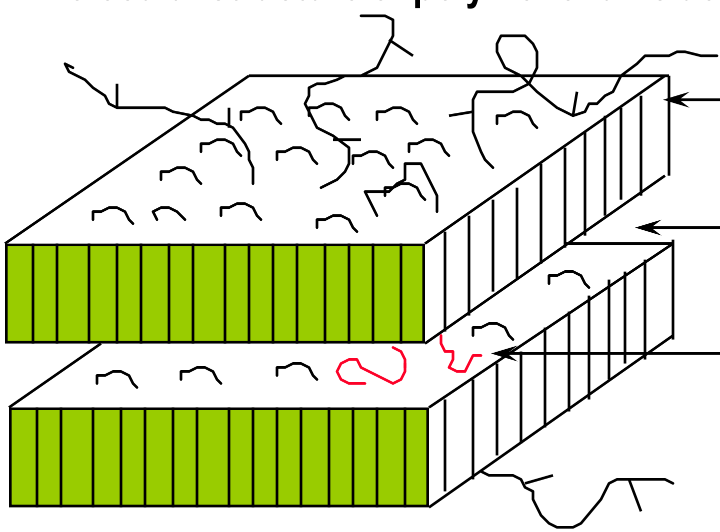



Polymer Properties Determined by Catalysis

Composition and molecular structure of each polymer chain determined by relative kinetic rates:



Molecular structure of polymer chains determines bulk structure:



Lamella: long sequences of ethylene units fold into crystallites

Interfacial regions: "defects" are excluded into amorphous regions

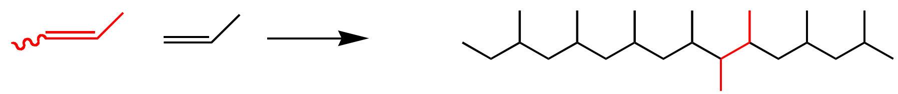
Tie molecule: Bridge more than one lamellar crystallite

Catalysis → Molecular Structure → Bulk Structure → Properties

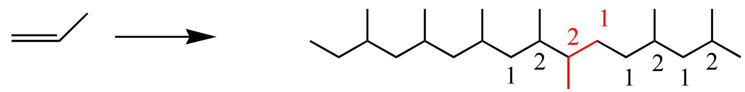
Controlling Microstructure via Catalysis

Polyolefin catalysts are some of the most powerful man-made catalysts invented!

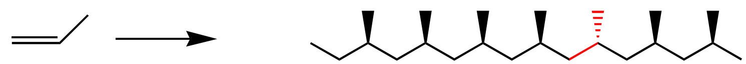
Chemoselectivity > 10^3:1



Regioselectivity > 10^2:1



Stereoselectivity ca. 10^2:1



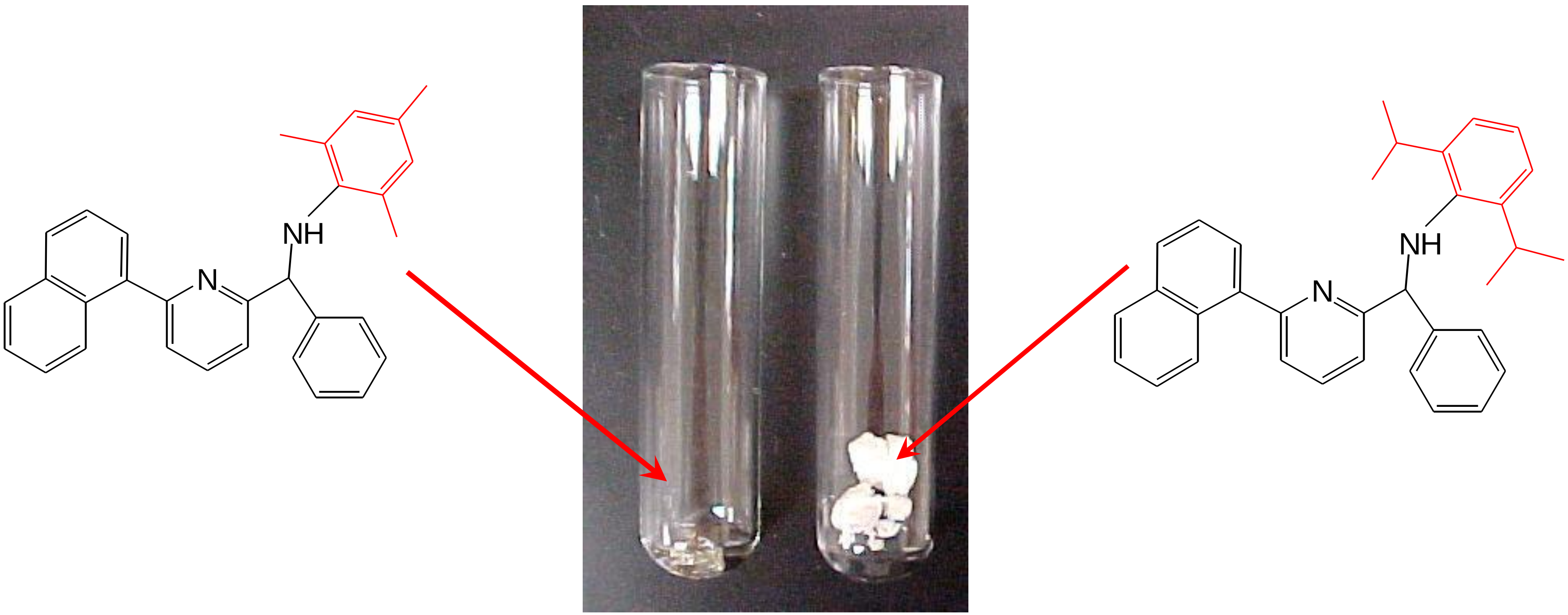
Catalytic rates: ~10^4 - 10^5 sec^{-1} (compare to enzymes, ~10^2–10^5 sec^{-1})

Productivity: Can be >10^8 T/O in 10 minutes

Thanks to Prof. Clark Landis

Control of polymer microstructure requires a mastery of the underlying kinetics

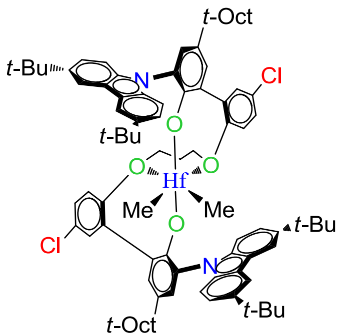
Minor Changes have Major Implications



- These two ligands resulted in catalysts which made two very different polymers.
- High Mw, crystalline iPP on the right; low Mw, low tacticity PP on the left.
  - Identification of catalyst structure-function relationships can be greatly accelerated by the use of High Throughput techniques

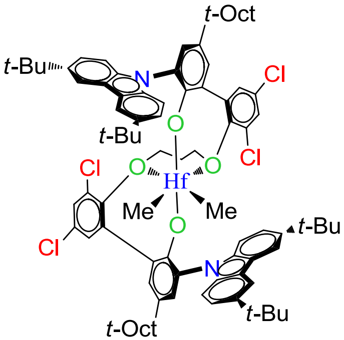
Controlling Comonomer Incorporation

Tailor the kinetic reactivity ratio of your catalyst for optimal flexibility.

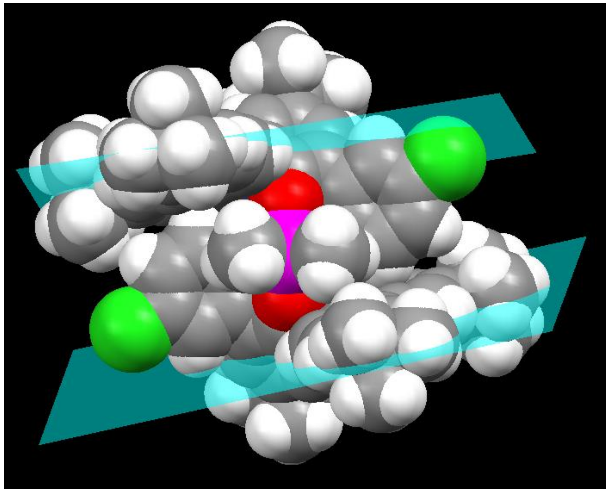


31.3 mol%
Tm = -24.5°C

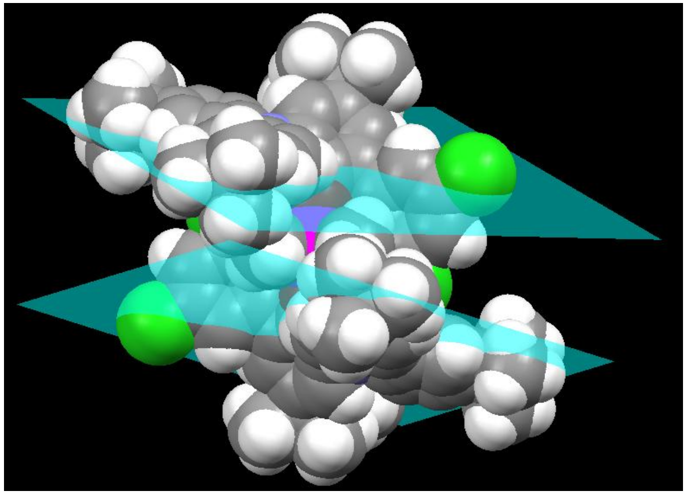
Batch ethylene-octene copolymerization



3.5 mol%
Tm = 101°C



dihedral angle = -19.0°

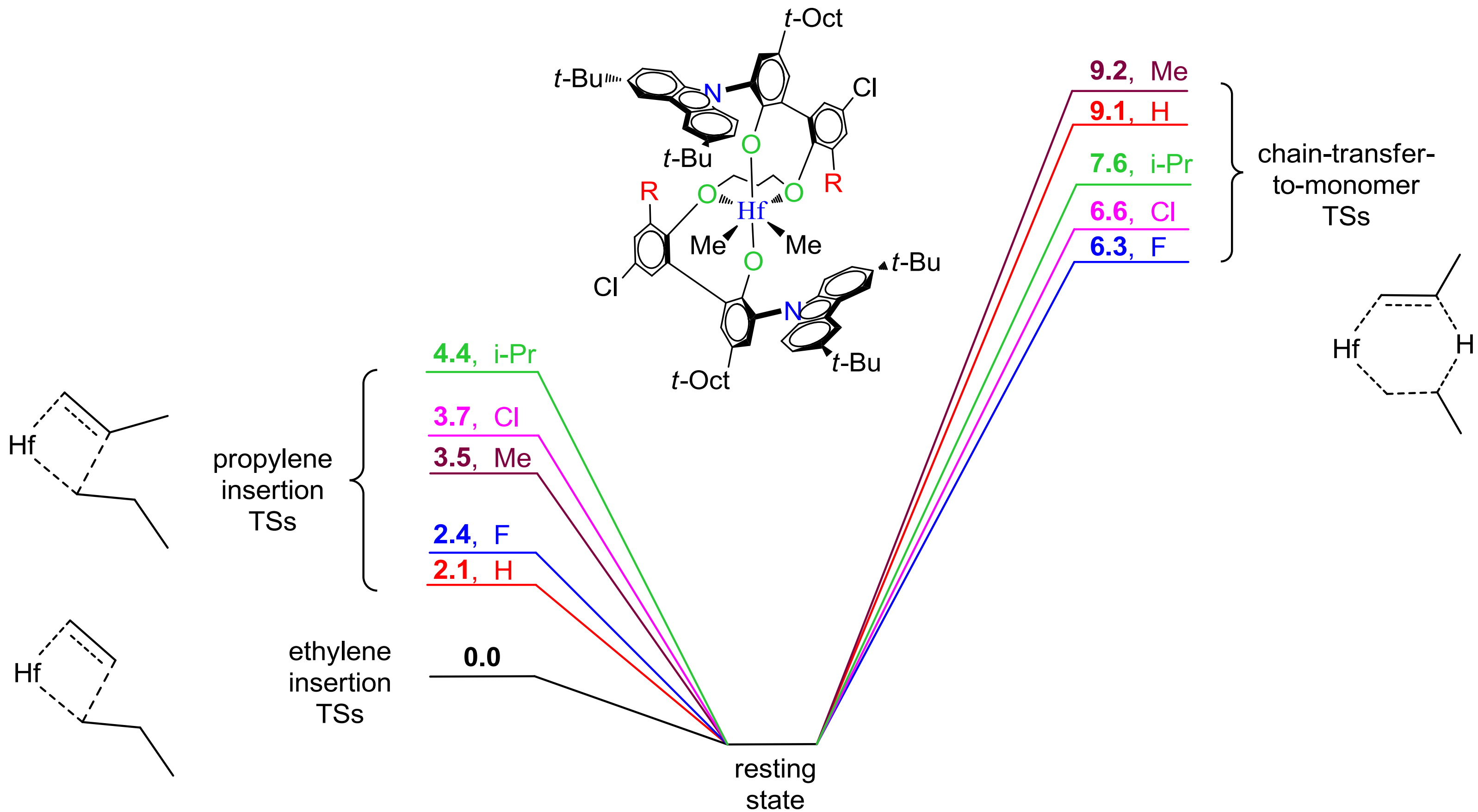


dihedral angle +28.9°

Dr. Jerzy Klosin

Calculations can Guide Synthesis

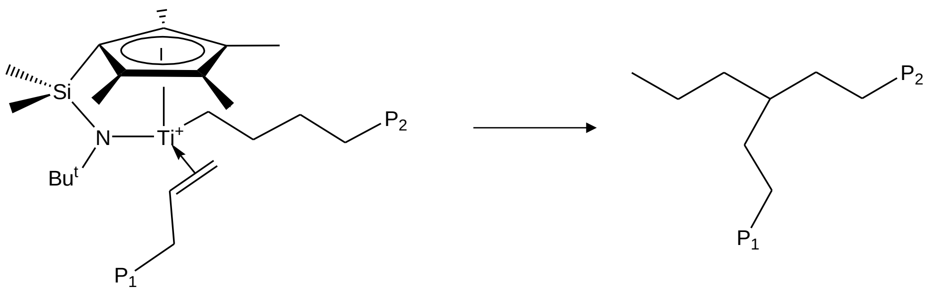
- DFT calculations help guide catalyst families toward the desired α–Olefin Incorporation and Mw Selectivities



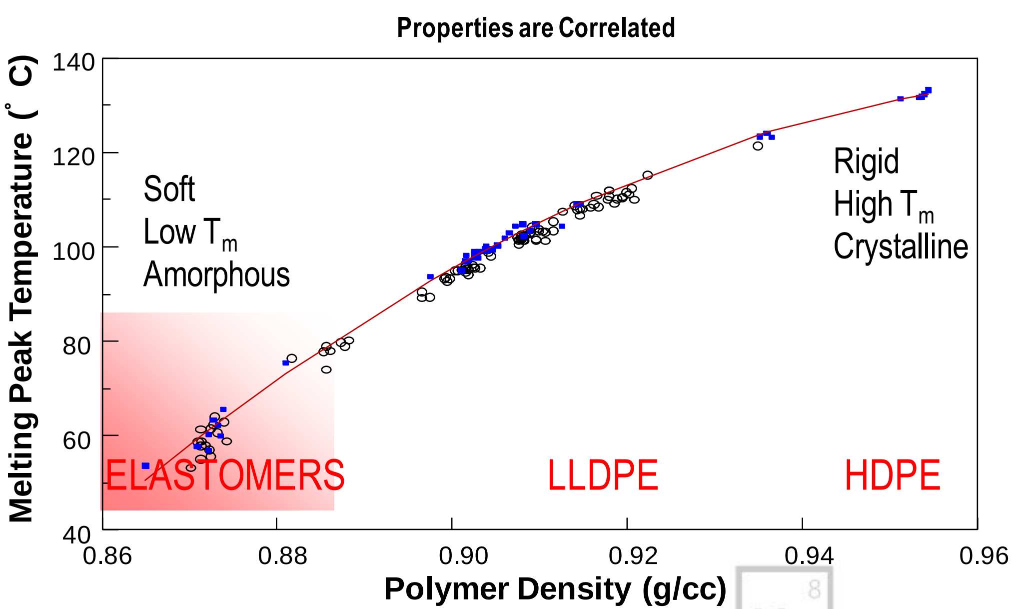
Dr. Robert Froese

“Single Site” Catalysts Have Limits

- Even “perfect” kinetic control of a single molecular catalytic site results in structural compromises limiting the applications of your resin.

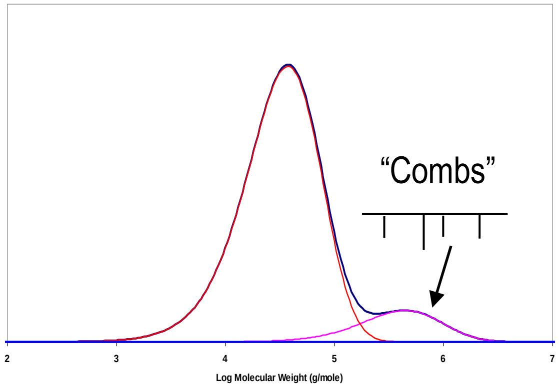


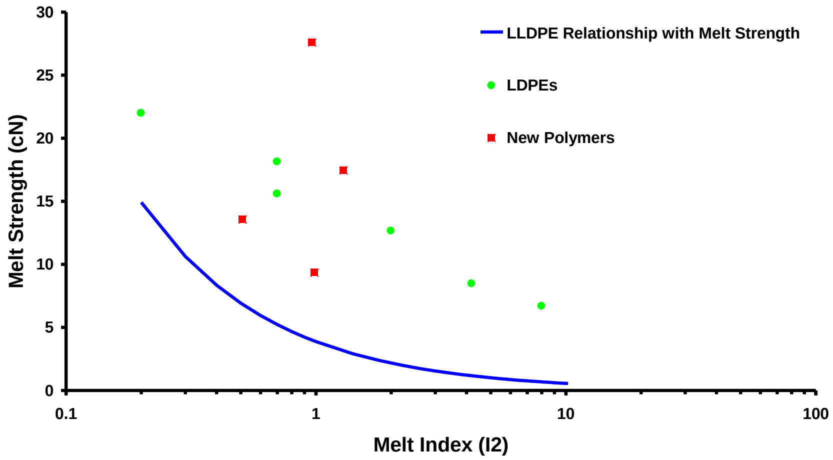
For a single-site catalyst system, the branches have the same Mw as the “backbone,” which can correlate rheology and mechanical properties.



Statistical (e.g. 1st order Markovian) comonomer distribution correlates modulus and melting point.

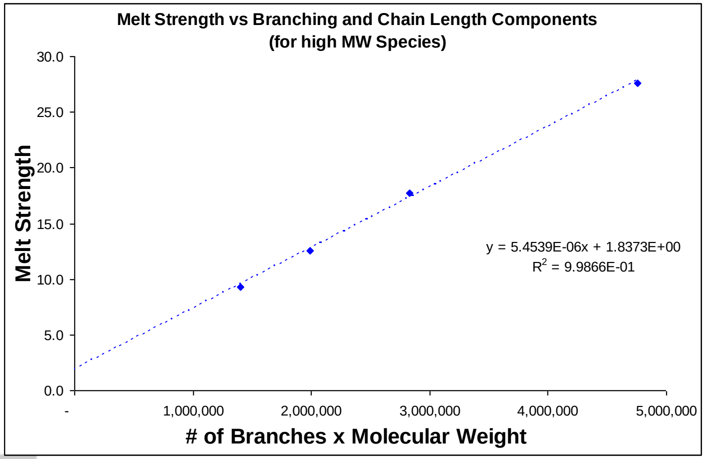
Control Size and Distribution of LCB



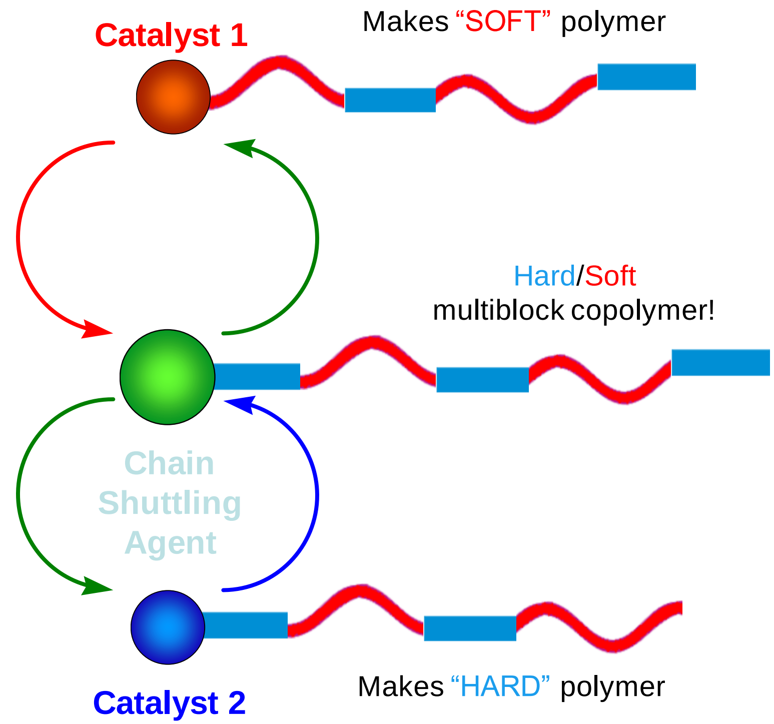


Dual catalyst technology to place comb molecules in the high molecular weight tail.
(See, e.g. Dow US patents 7,999,039; 7,300,983; 6,875,816; 6,942,342.)

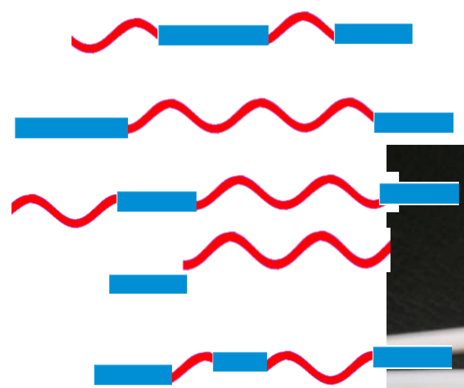
Tandem catalysis can be used to "dial in" melt strength by adjusting the concentration of comb molecules

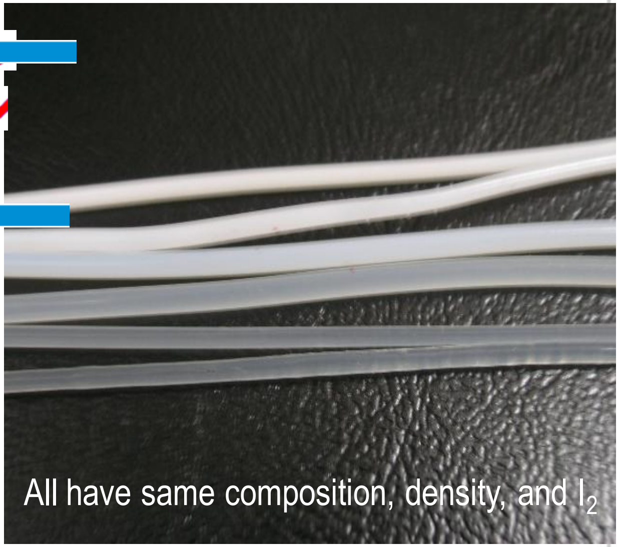


OBCs by Chain Shuttling Catalysis



Chain shuttling generates a HARD/SOFT multiblock copolymer.
Note: Not stoichiometric in CSA!

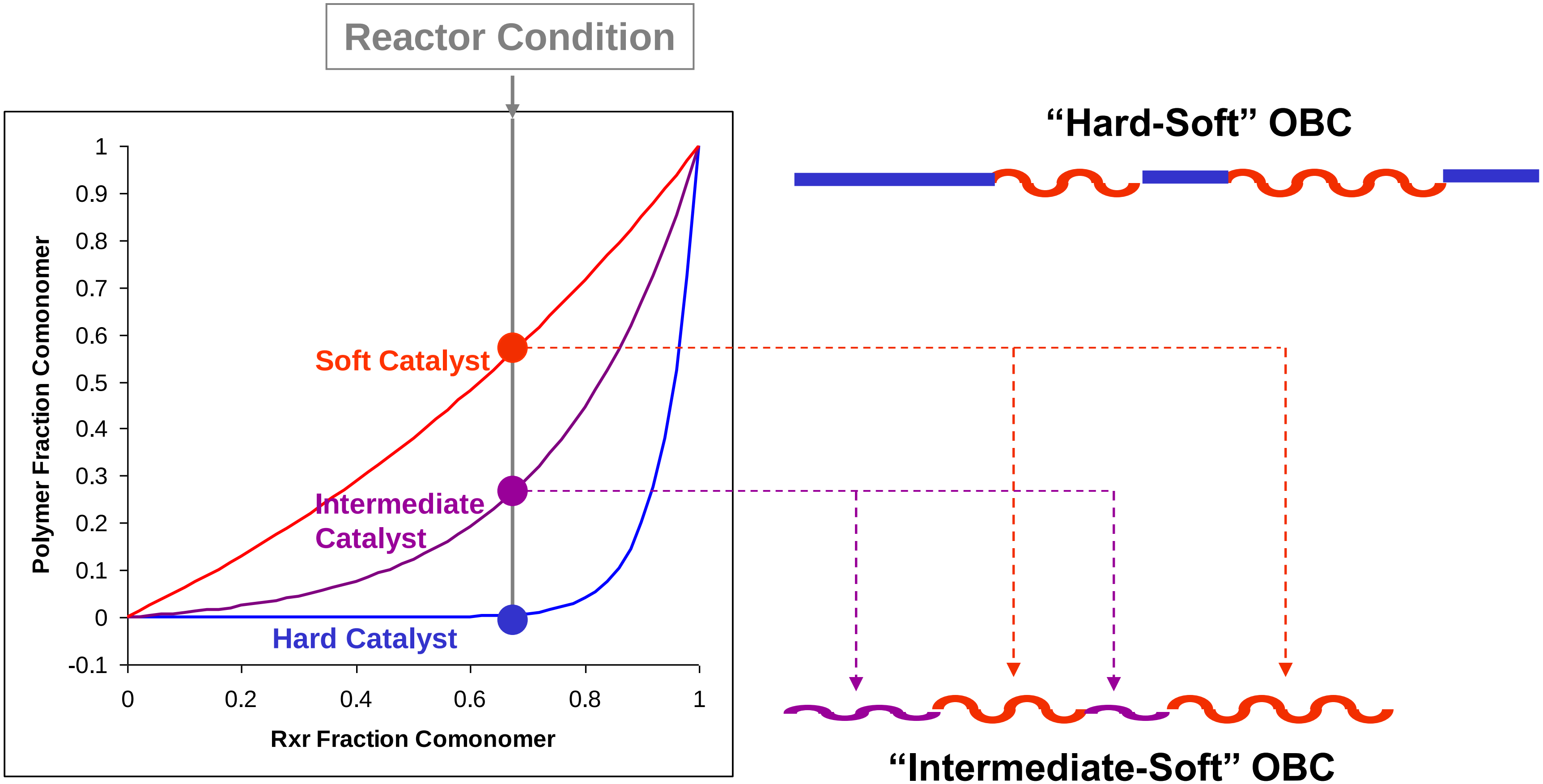




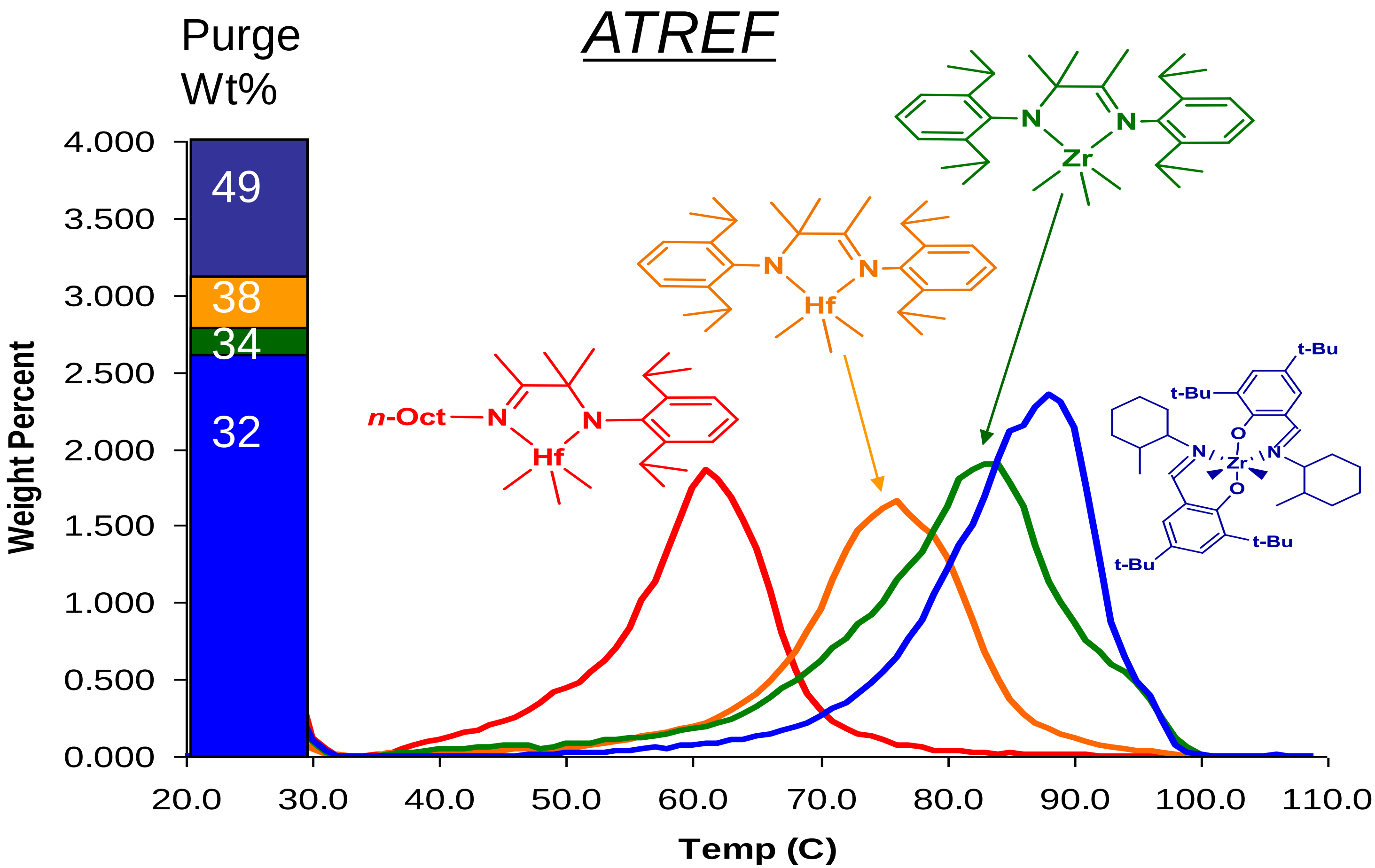
Breaks correlation between modulus and melting point!

Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science* 5 May 2006: 714.

Controlling the OBC Density Split



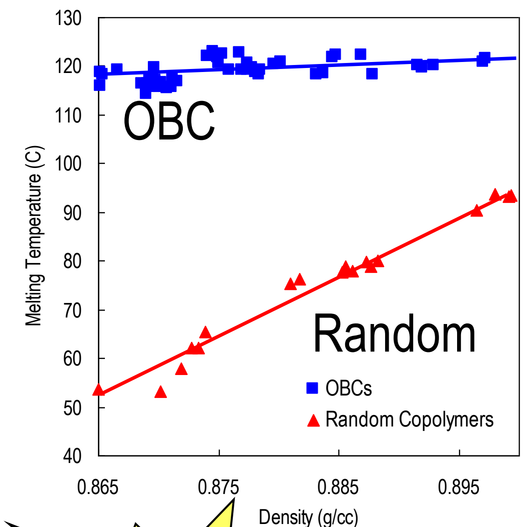
New Catalysts Can Tune the Comonomer Content of the Hard Block



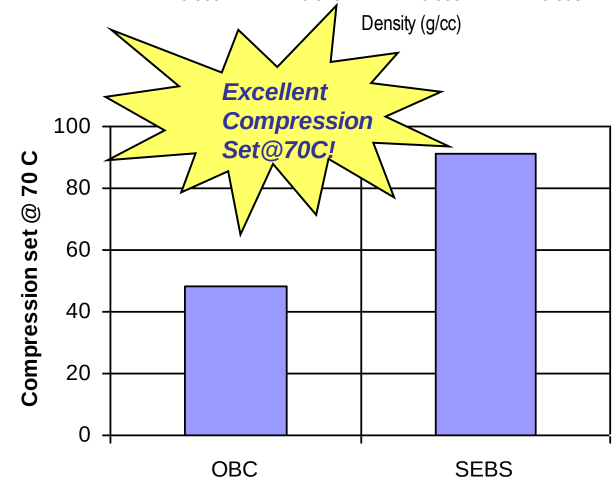
Kuhlman, R. L.; Klosin, J. *Macromolecules*, 2010, *43*, 7903.

Commercialized by Dow as INFUSE™ OBCs

- Outstanding flexibility-high temperature resistance balance
- Fast set-up in processing (shorter cycle time) – soft compounds!

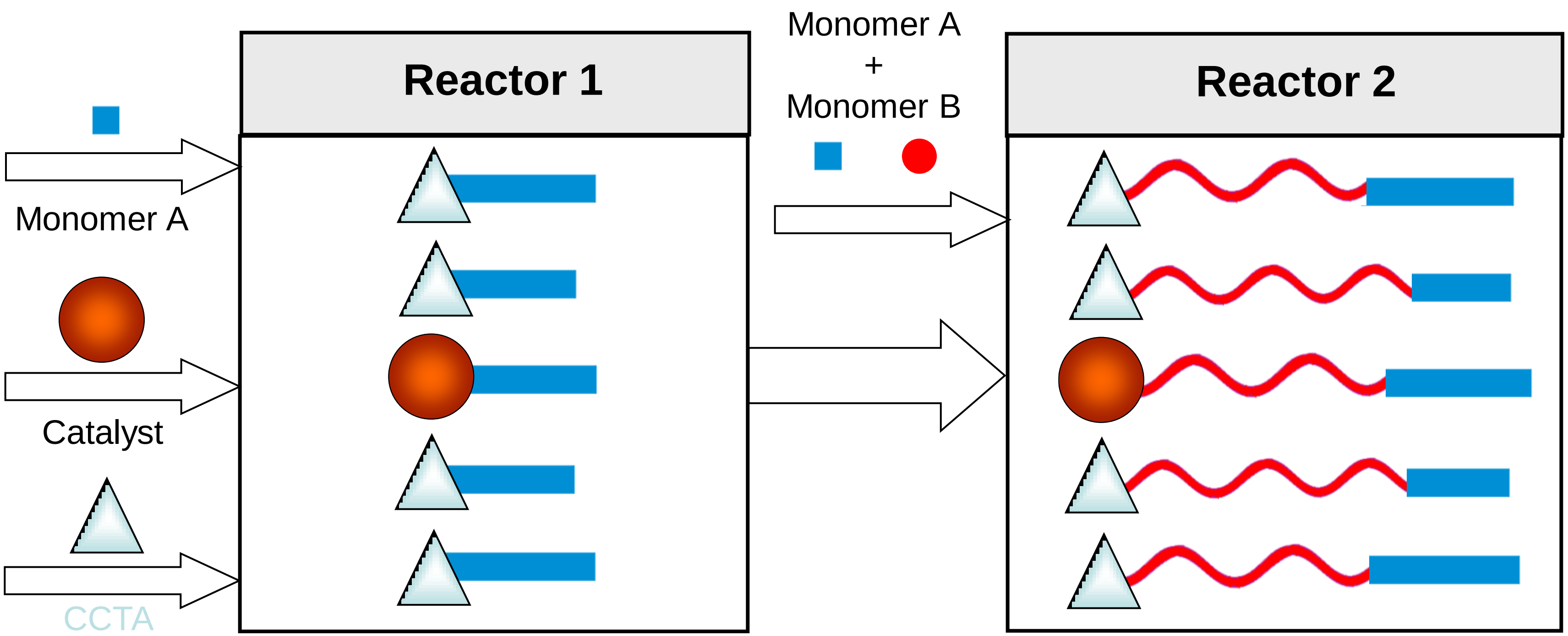


- Excellent elastic recovery properties
- Good compression set performance at room and elevated temperatures



TM Trademark of The Dow Chemical Co

Dual Reactor CCTP Concept: Sequential Monomer Addition



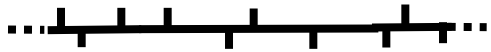
Coordinative chain transfer agent

CCTP generates HARD/SOFT diblock!

Hustad, Kuhlman, Arriola, Carnahan, Wenzel *Macromolecules*, **2007**, *40*, 7061 .

A New Level of Microstructure Control

Random Copolymer



- Billions of pounds made and sold world-wide
- “Best” materials are statistically random (kinetic control)

- From random copolymers to statistical multiblocks. ✓

Statistical Multiblock

Hard blocks

- Statistical multiblocks with excellent heat/elasticity balance
- Commercialized as INFUSE™ Olefin Block Copolymers

See: *Science*, **2006**, 312, 714.

- Statistical diblocks by coordinative chain transfer polymerization. ✓

Statistical Diblock

Hard block

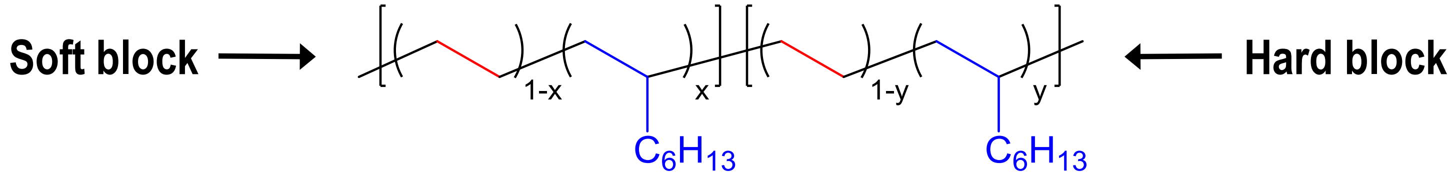
- Exactly two blocks per chain
- Statistical distribution of block lengths

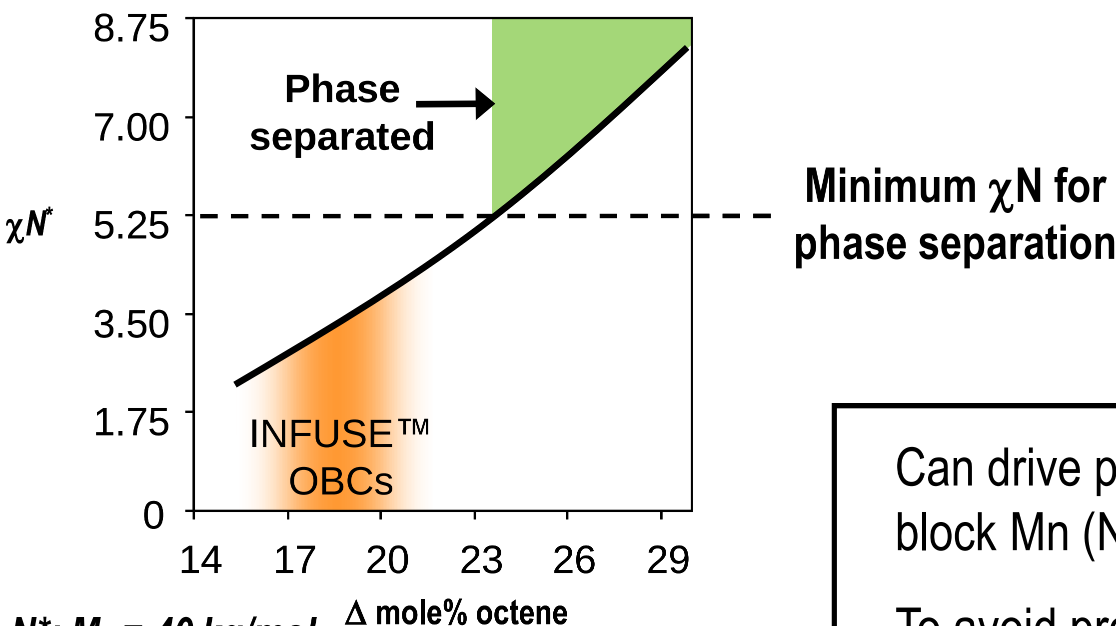
See: *Macromolecules*, **2007**, *40*, 7061.

Is this as far as we can push polyethylene performance?

No! Molecular structure can also determine melt-state thermodynamic phase behavior.

Design OBCs to Phase Separate in the Melt





N*: M_n = 40 kg/mol

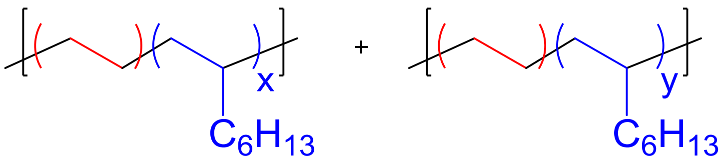
50% hard segment

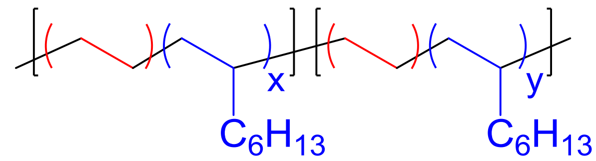
Modeling: Jeff Weinhold

Can drive phase separation by increasing block Mn (N*) or incompatibility (χ).

To avoid processing issues, we chose to increase octene in the soft block.

Ordered Morphologies Observed





Physical Blend

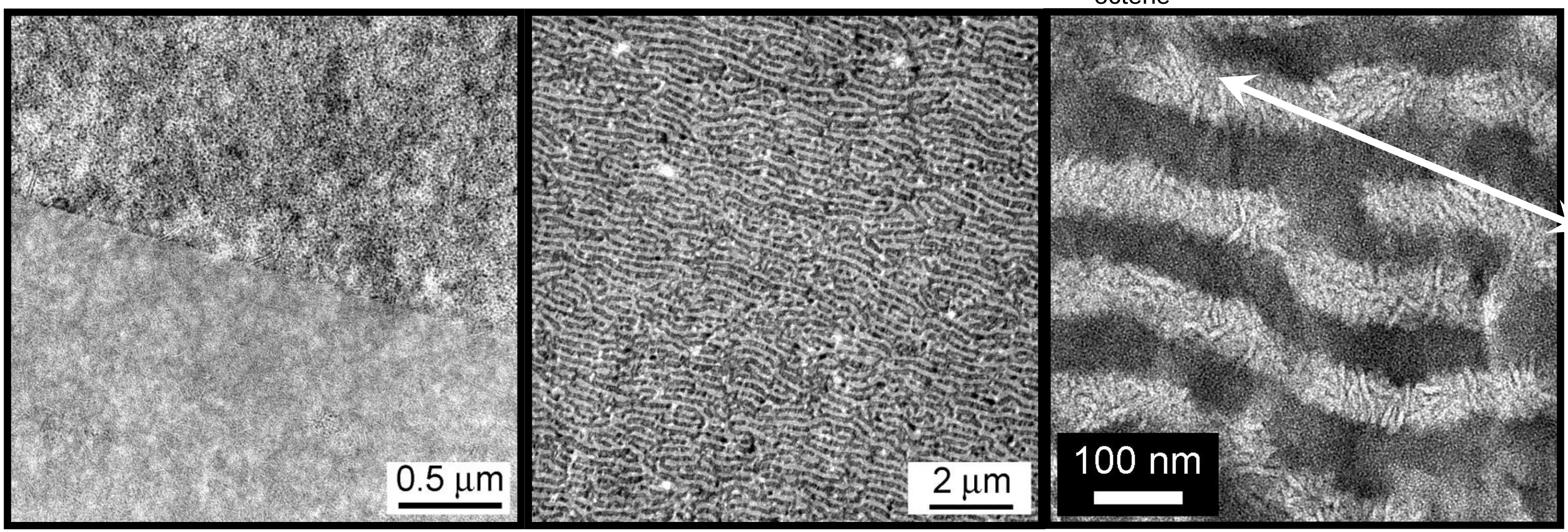
M_n = 45 kg/mol, PDI = 4

Δ_{octene} = 40

High Octene OBC

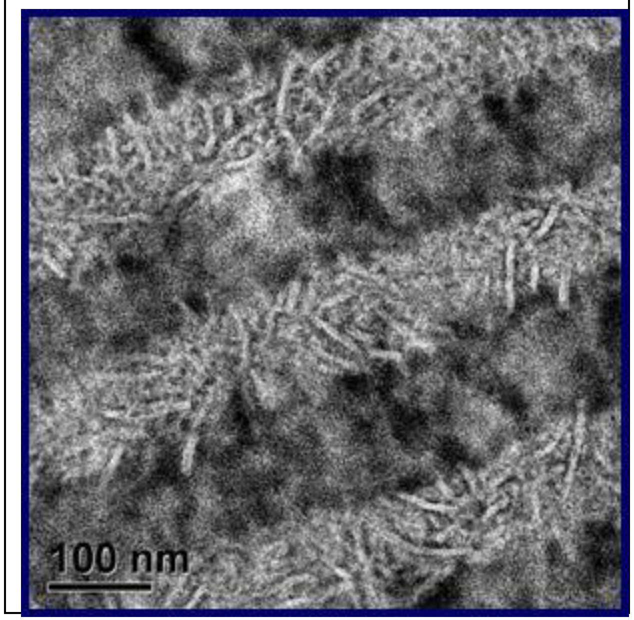
M_n = 47 kg/mol, PDI = 2

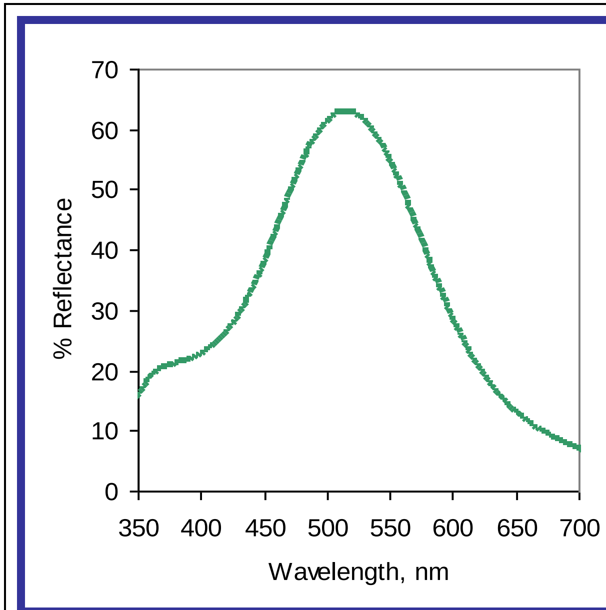
Δ_{octene} = 36

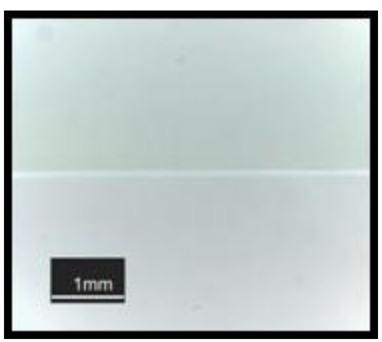


Hustad, Marchand, Garcia-Meitin, Roberts, Weinhold *Macromolecules* **2009**, *42*, 3788

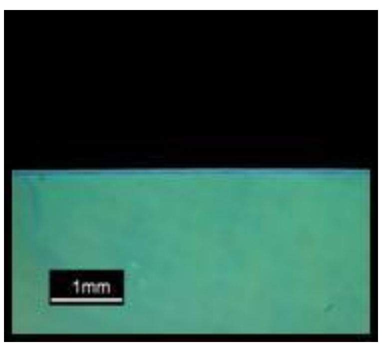
Simple Pressed Plaques Scatter Blue Light



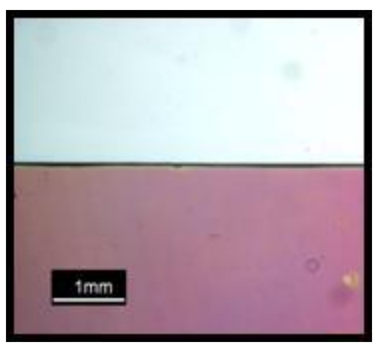




Reflected light on solid white plate

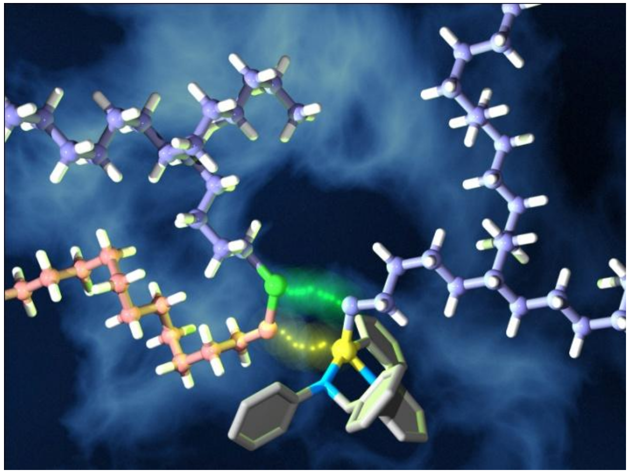


Reflected light on solid black plate



Transmitted Light thru clear glass plate

Innovation in Polyolefins Requires a New Level of Microstructural Control

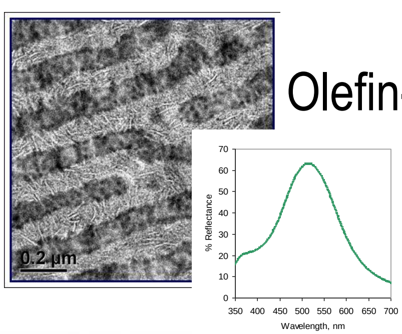


Mastery of catalyst structure-function relationships to tune polymer properties is critical.

Achieving new combinations of properties from the same mixture of olefins requires even more elegant catalyst solutions.

Statistical multiblocks

INFUSE™
OLEFIN BLOCK COPOLYMERS



Olefin-based advanced Optical materials

Statistical diblocks

...and beyond.

Acknowledgments

Core R&D

Dan Arriola

Rob Froese

Phil Hustad

Roger Kuhlman

Jeff Weinhold

Tim Wenzel

Analytical

Eddy Garcia-Meitin

Dow Elastomers

Tom Karjala

Colin Li Pi Shan

Gary Marchand

Kim Walton

Pilot Plants

Jan Bazen

Curvel Hypolite

Christine Westgate

… and many more.