Technology Driven Innovation in Plastics

Custom Polyolefins by Molecular Design

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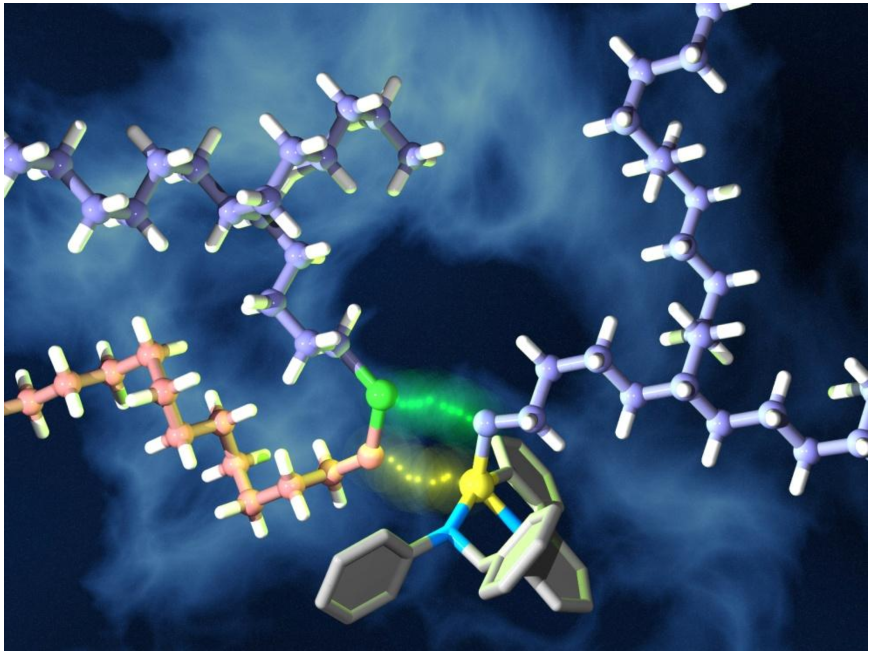


Polyethylene is Everywhere

- Global demand exceeds 120 Billion pounds per year!
- 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

Custom Polyolefins

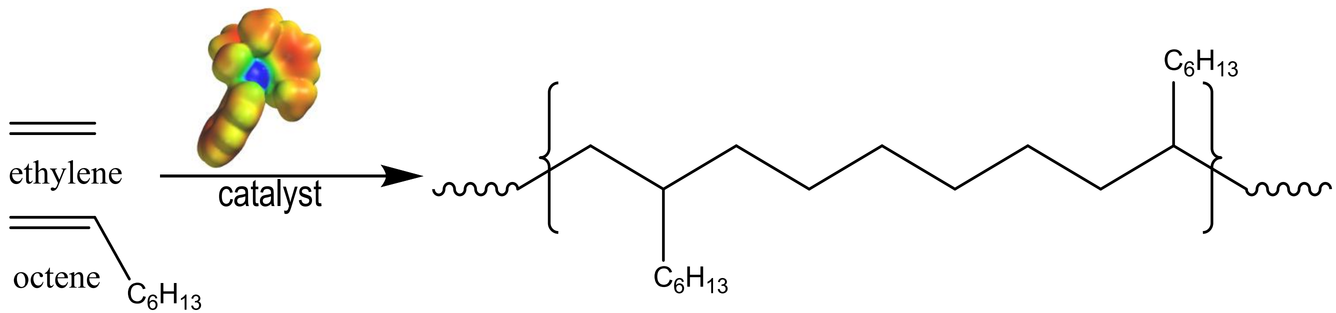
- Polyolefins are often considered first to use in any application
  - Excellent cost / performance value
  - Ease of recycling 

  - Low energy to process and fabricate into films, parts, etc.

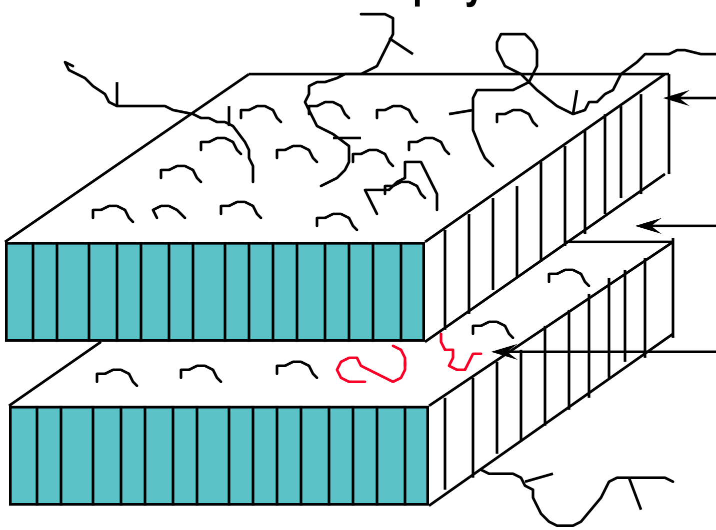
- State of the Business in 1990
  - Industry-wide overcapacity and low profitability
  - Producers discussing exit strategies such as mergers and outright sales of assets
    - Feeling that the big discoveries had already been made in this area
    - Feeling that the future belonged to those with low cost energy and feedstocks

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

Two Important Discoveries in Basic Science Funded by DOE Office of Basic Energy Sciences

Organometallics **1990**, *9*, 867–869 867

$[\{(\eta^5\text{-}C_5Me_4)Me_2Si(\eta^1\text{-}NCMe_3)\}(PMe_3)ScH]_2$: A Unique Example of a Single-Component α-Olefin Polymerization Catalyst†

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Received November 6, 1989

Summary: The synthesis and structure of the title compound are described. $[\{(\eta^5\text{-}C_5Me_4)Me_2Si(\eta^1\text{-}NCMe_3)\}Sc(PMe_3)]_2(\mu\text{-}H)_2$ (**3**) crystallizes with a molecule of toluene per scandium in the monoclinic system, space group $C2/c$, with a = 21.238 (3) Å, b = 11.470 (2) Å, c = 22.253 (3) Å, β = 113.16 (1)°, V = 4984.0 (14) Å^3, Z = 8 (four dimers), and d = 1.24 g·cm^{-3}. Propene, 1-butene, and 1-pentene are cleanly, albeit slowly, polymerized with >99% "head-to-tail" coupling to produce linear, atactic polymers with M_n = 3000–4000 and PDI's of 1.7–2.1. Chain transfer is relatively slow and appears to occur by β-H elimination. All evidence points to a one-component catalyst system with all scandium centers functioning alike.

Despite the tremendous importance of Ziegler–Natta olefin polymerization,[2] the structures of the catalysts have remained elusive. Direct characterization is complicated by their multicomponent composition, and normally only a small percentage of the transition-metal centers are active.[3]

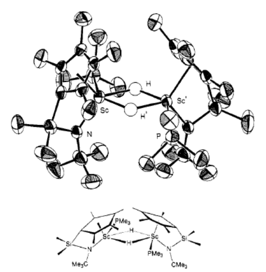

Figure 1. ORTEP drawing of $[(Cp^*SiNR)Sc(PMe_3)]_2(\mu\text{-}H)_2$ (3). Thermal ellipsoids are shown at the 50% probability level; methyl hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Sc–P, 2.996 (1); H–H', 2.13 (4); ring centroid–Sc–N, 104.8 (3); H–Sc–H', 65.9 (10); H–Sc–P, 68.8 (7); N–Sc–P, 95.3 (1).

Sc–R, and $\{(\eta^5\text{-}C_5H_3CMe_3)_2SiMe_2\}$Sc–R undergo facile olefin insertion and β-H and β-alkyl elimination, elementary transformations pertinent to Ziegler–Natta catalysis.[5] The striking effect on the reactivity of the scandium center

J. Am. Chem. Soc. **1991**, *113*, 3623–3625 3623

CUP2 spectrum also closely resembles that of the Cu(I) cluster in *N. crassa* metallothionein as well as those of several other metallothioneins,[23-24] most notably the *Saccharomyces cerevisiae* yeast metallothionein itself.[4] The edge energy position, along with the absence of a 1s → 3d transition, further establishes that it is indeed a Cu(I), and not a Cu(II), cluster.[20]

Taken together, the results thus suggest that CUP2 contains Cu atoms arranged in a cluster bridged by S atoms, presumably donated by protein cysteines. The Cu–S distance (2.26 Å) and coordination numbers determined from EXAFS are consistent with the electronic structure indicated by the edge transition. It is furthermore consistent with findings from Cu–S model clusters, where two-coordinate Cu–S distances average 2.16–2.17 Å, trigonal coordination 2.25–2.28 Å, and tetragonal coordination 2.3–2.42 Å.[17,25] CUP2 thus joins the class of Cu–S cluster-containing proteins, established through EXAFS in the metallothioneins of *S. cerevisiae* yeast,[4] *N. crassa* fungus,[16] β-domain of rat liver,[22] a mixed Cu:Zn metallothionein from pig liver,[23] and possibly also canine liver[24] (although in this study, the Cu–S distance was 2.27 Å but the coordination number four).

It is thus remarkable that the CUP2 copper cluster seems to resemble that of the very yeast metallothionein protein[4] that it regulates. What is the functional advantage for CUP2 to be activated by formation of a copper cluster, instead of a simple mononuclear copper center? There are several possibilities. A small amount of copper is necessary for viability of yeast, but high concentrations are deleterious. Induction of metallothionein synthesis could be controlled to a fine degree of cooperative construction of a copper cluster in CUP2 . Thiolate-bridged clusters are characteristic of copper(I) chemistry and offer a way to enforce specificity for copper in metallothionein activation. Effective DNA binding might require more than one structural domain to be formed in a protein. Although the zinc finger is

"Cation-like" Homogeneous Olefin Polymerization Catalysts Based upon Zirconocene Alkyls and Tris(pentafluorophenyl)borane

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Received December 17, 1990

Lewis acid cocatalysts such as aluminum alkyls and methylalumoxane are ubiquitous components of several important classes of highly active group 4 alkyl-based (e.g., titanocene, zirconocene) olefin polymerization catalysts.[1,2] Although electrodialysis,[3] chemical trapping,[4] model synthetic,[5-7] XPS,[8] surface chemical,[9] NMR spectroscopic,[10] and theoretical studies[11] argue indirectly that the role of the Lewis acid is to promote (e.g., by alkide abstraction) the formation of unsaturated "cation-like" active centers (e.g., Cp_2MR^+), the exact structural nature of the catalyst–cocatalyst interaction has remained elusive. We report here the use of the strong Lewis acid tris(pentafluorophenyl)borane[12] for the first synthesis of stoichiometrically precise, isolable/crystallographically characterizable, highly active "cation-like" zirconocene polymerization catalysts.

(1) For recent reviews of transition-metal-centered olefin polymerization catalysis, see: (a) Quirk, R. P., Ed. *Transition Metal Catalyzed Polymerizations*; Cambridge University Press: Cambridge, 1988. (b) Kaminsky, W., Sinn, H., Eds. *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*, Springer: New York, 1988. (c) Keii, T., Soga, K., Eds. *Catalytic Polymerization of Olefins*; Elsevier: Amsterdam, 1986. (d) Pino,

- Prof. John Bercaw – Caltech
- Poor catalyst but provided important new information on catalyst structure
- Grant # DE-FG03-85 ER13431
- Published in *Organometallics*

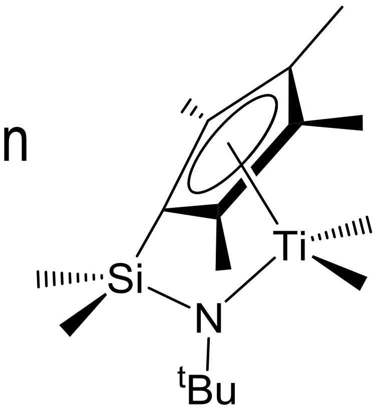
- Prof. Tobin Marks – Northwestern
- New idea for activators for catalysts
- Grant # DE-FG02-86 ER13511
- Published in *Journal of the American Chemical Society*

Innovation Process – be the first to:

- Acquire new knowledge through research
- Apply the knowledge to create a sought-after product or service
- Introduce the innovation to the marketplace using entrepreneurship

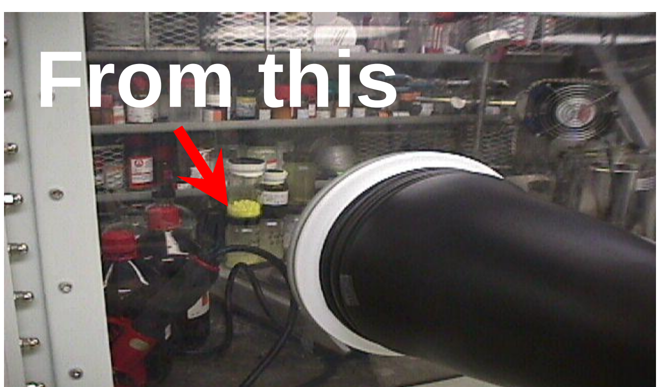
Dow Chemical Constrained Geometry Catalyst

- Over 400 people involved in commercialization
- >2 billion pounds/yr plastics and elastomers produced using INSITE catalyst
- Extremely efficient process for making elastomers
  - Less energy, less environmental impact, higher utilization of resources



+ $B(C_6F_5)_3$

Constrained Geometry Catalyst (CGC)

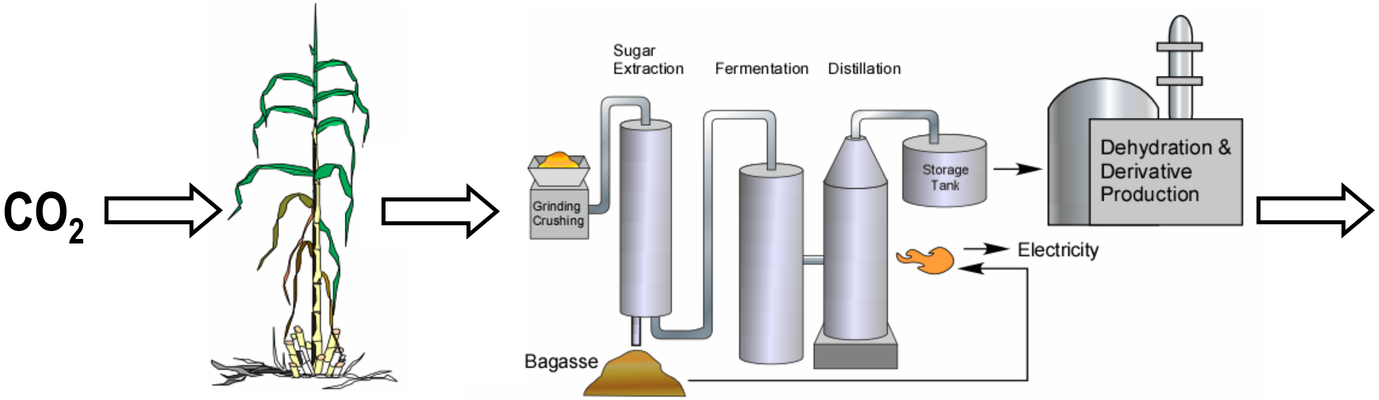


Polyolefin Products Launched Using New Catalysts

AFFINITY* Polyolefin Plastomers	1993
ENGAGE* Polyolefin Elastomers	1994
ELITE* Enhanced Polyethylene	1996
NORDEL*IP EPDM (Solution Process EPDM)	1996
AFFINITY* Adhesives	1998
INDEX* Interpolymers	1999
Thermoplastic Polyolefins (TPO's)	2000
INSPIRE* Performance Polymers	2000
Gas Phase Polyethylene (Sold to BP)	2001
Slurry Phase Polyethylene (Sold to Univation)	2001
DOW XLA* Elastic Fibers	2002
NORDEL* MG EPDM (Gas Phase EPDM)	2002
VERSIFY* Propylene Plastomers and Elastomers	2004
INFUSE* Olefin Block Copolymers	2007

Polyolefins are now bio-polymers!

Bio-Ethanol to Polyethylene

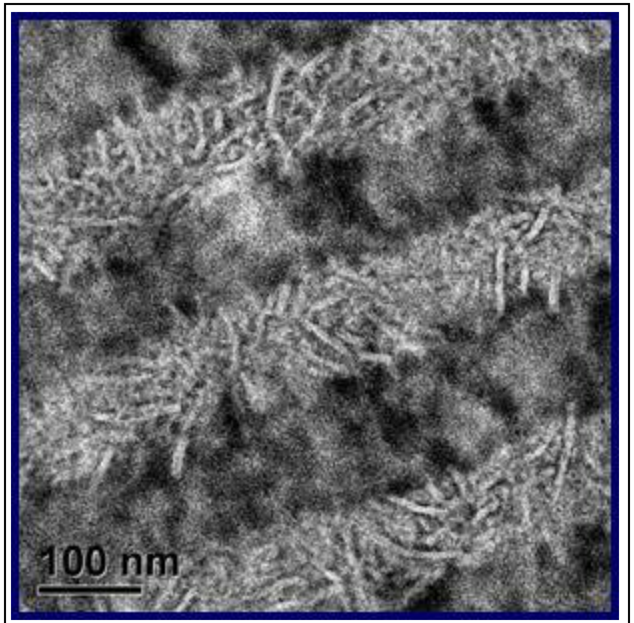


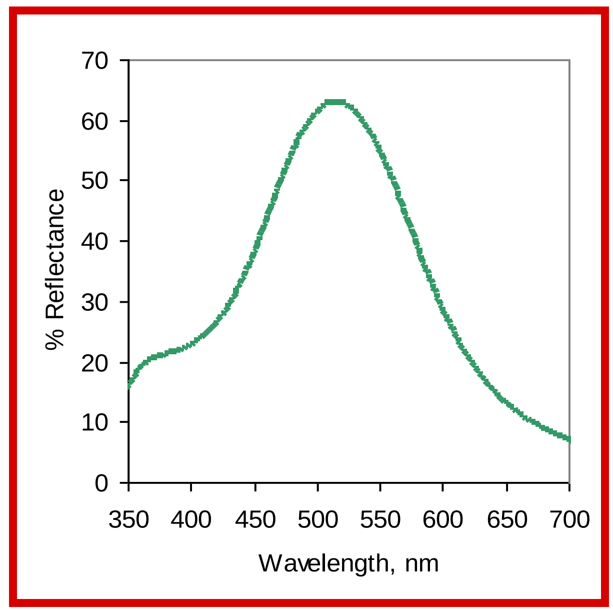
$$\text{“}CH_2O\text{”} \xrightarrow{\text{fermentation}} CH_3CH_2OH \xrightarrow[\text{dehydration}]{\text{catalytic}} CH_2{=}CH_2 + H_2O \longrightarrow \text{Polyethylene}$$

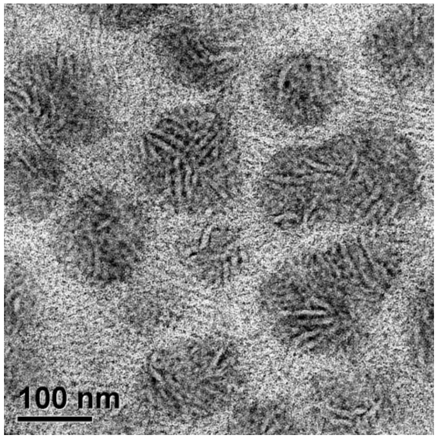
- 700 Million pounds per year of Polyethylene
- 450 square miles of sugar cane in Brazil
- Recyclable plastic (CO_2 fixation)
- Cheaper than many fossil sources
- Lower capital footprint
- 8% of Dow LLDPE capacity
- Walled off from oil volatility

Dow is working with Algenol Biofuels, other contributors, and the DOE to build and operate a pilot-scale algae-based integrated biorefinery that will convert CO_2 into ethanol, then ethylene. This project uses salt water and non-arable land.

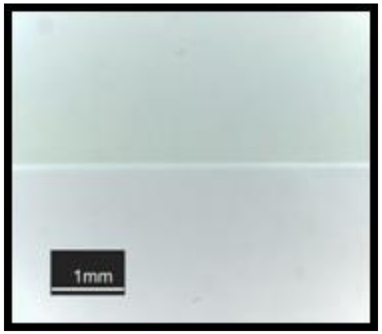
Manipulating Light with Self-Assembled Polyolefins



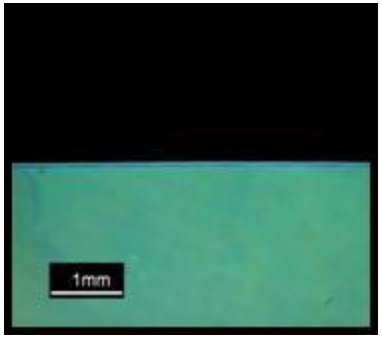




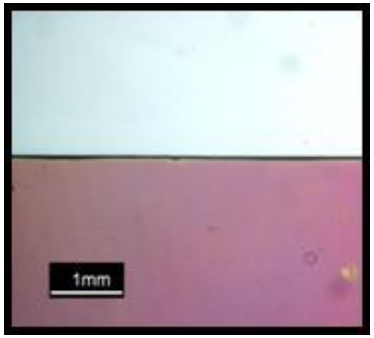
Nano-domain Ordering



Reflected light on solid white plate



Reflected light on solid black plate



Transmitted Light thru clear glass plate

Molded shapes, no color added

Everyday & Future Products Using INSITE* Technology

- Car bumpers, belts, window seals, and hoses
- Athletic shoes
- Crocs‡ shoes
- "Plastic" wine corks
- Electrical wire jackets
- "Comfort-stretch" clothing
- Roofing membranes
- Food packaging

Light, Energy Management

Security

* Trademark of The Dow Chemical Company

‡ Trademark of Crocs, Inc.