Lecture 29

May 2, 2019

Chemistry 328N

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- Ella Jiang
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- Jacob Sass

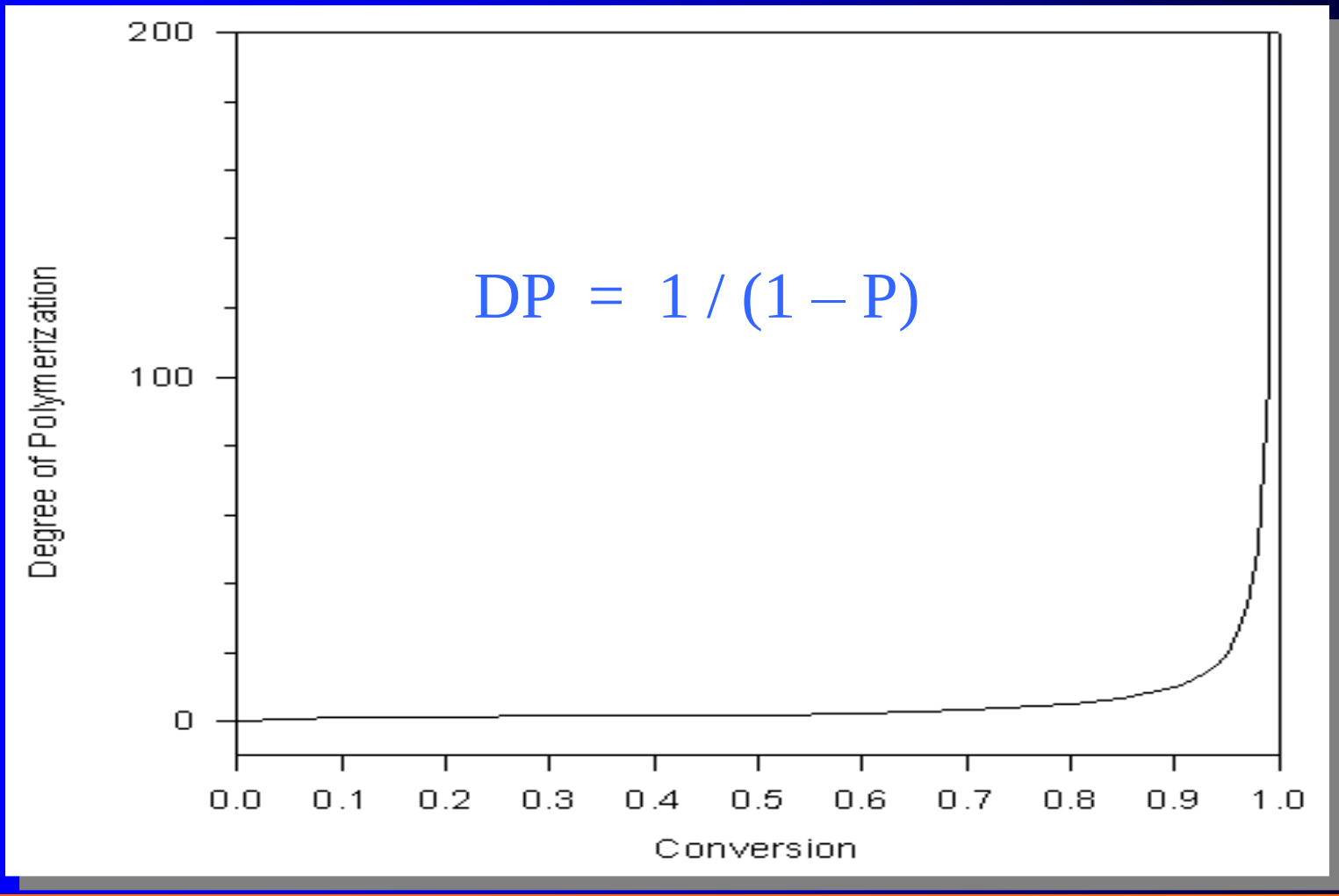
Final Exam

- Where: GSB 2.124!!
- When: Tuesday, May 21st , 9 AM – Noon
- Do: Study lecture notes, homework, reading
- Practice: Hydrolysis, signatures…and synthesis.
- Review: Spectroscopy and "unknowns"
- Please: Do a good job!

See web site for old exams

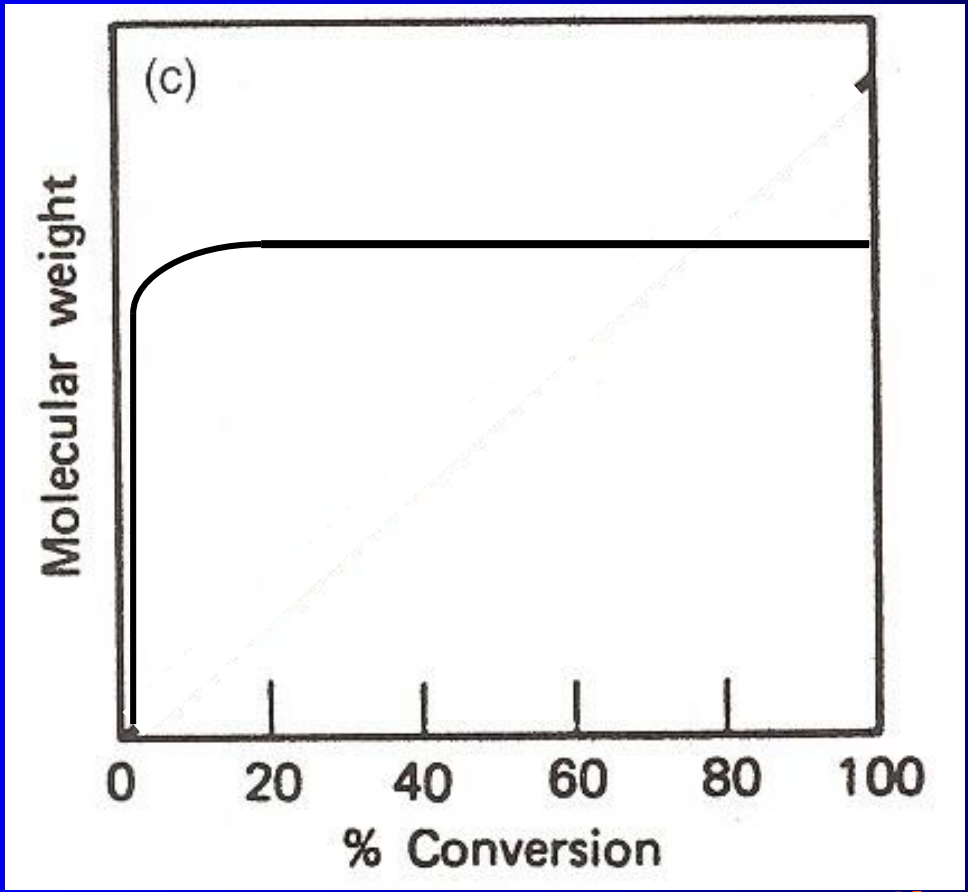
The step growth system

It all happens at the end!!!



The chain growth system

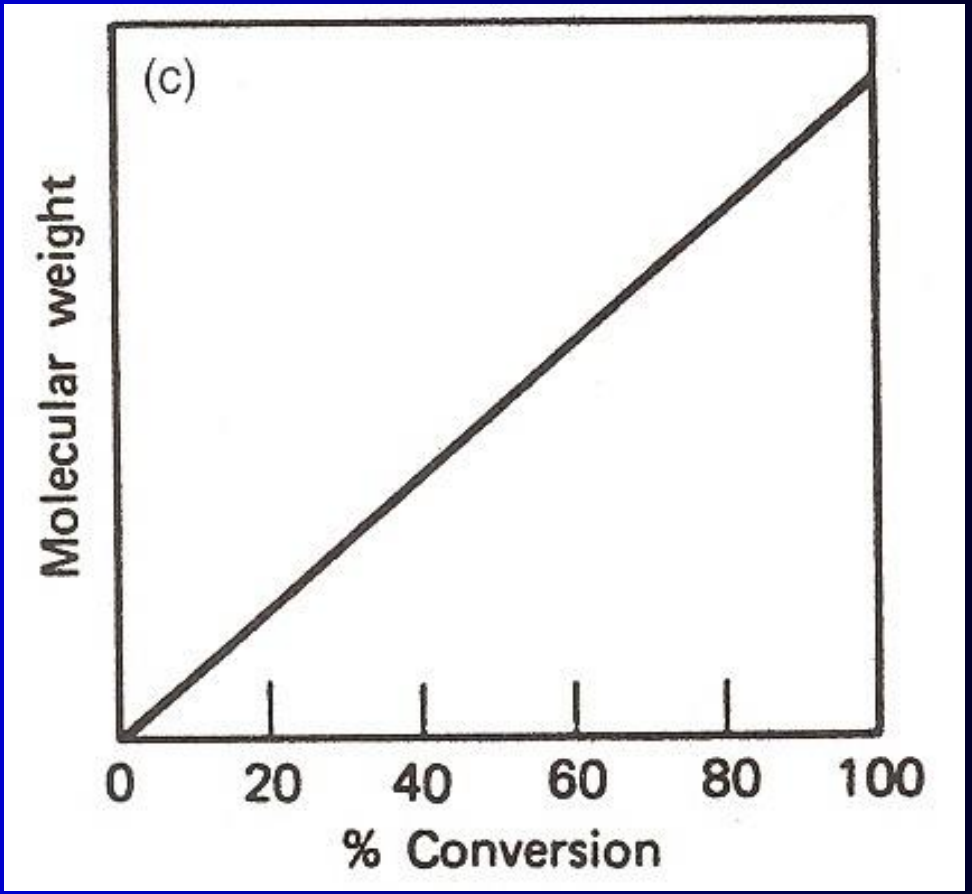
The relationship between DP and conversion
With termination reactions…steady state



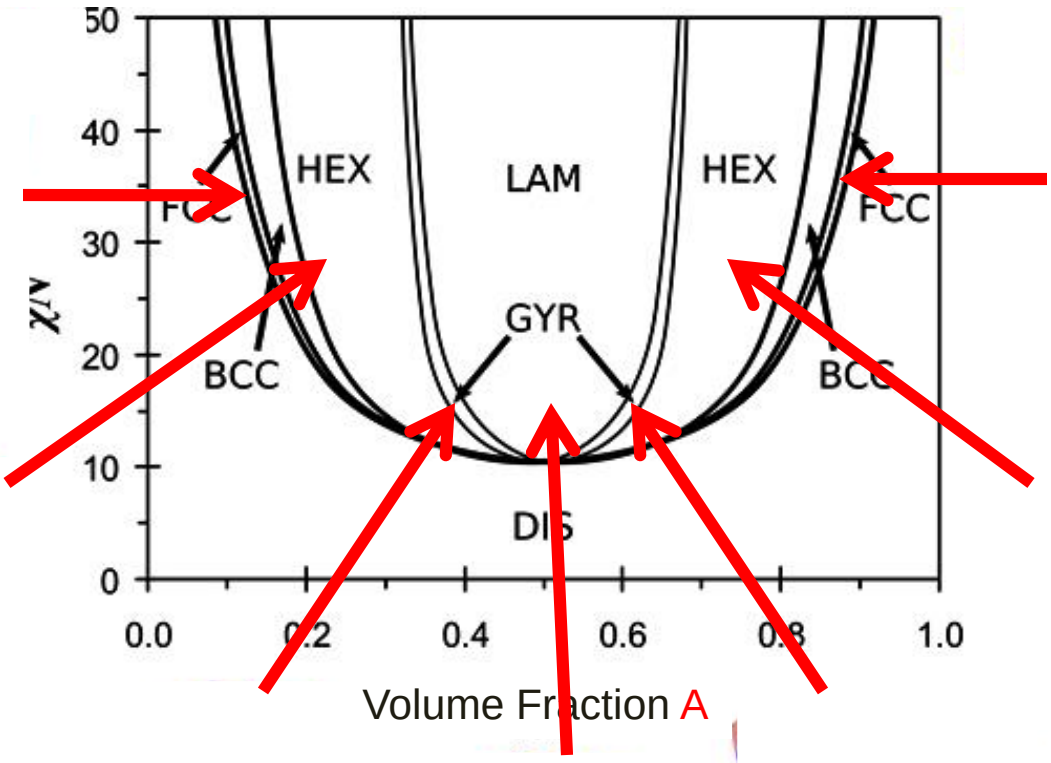
The Living Polymerization

$$DP_{t=\infty} = \frac{[M]}{[I]}$$

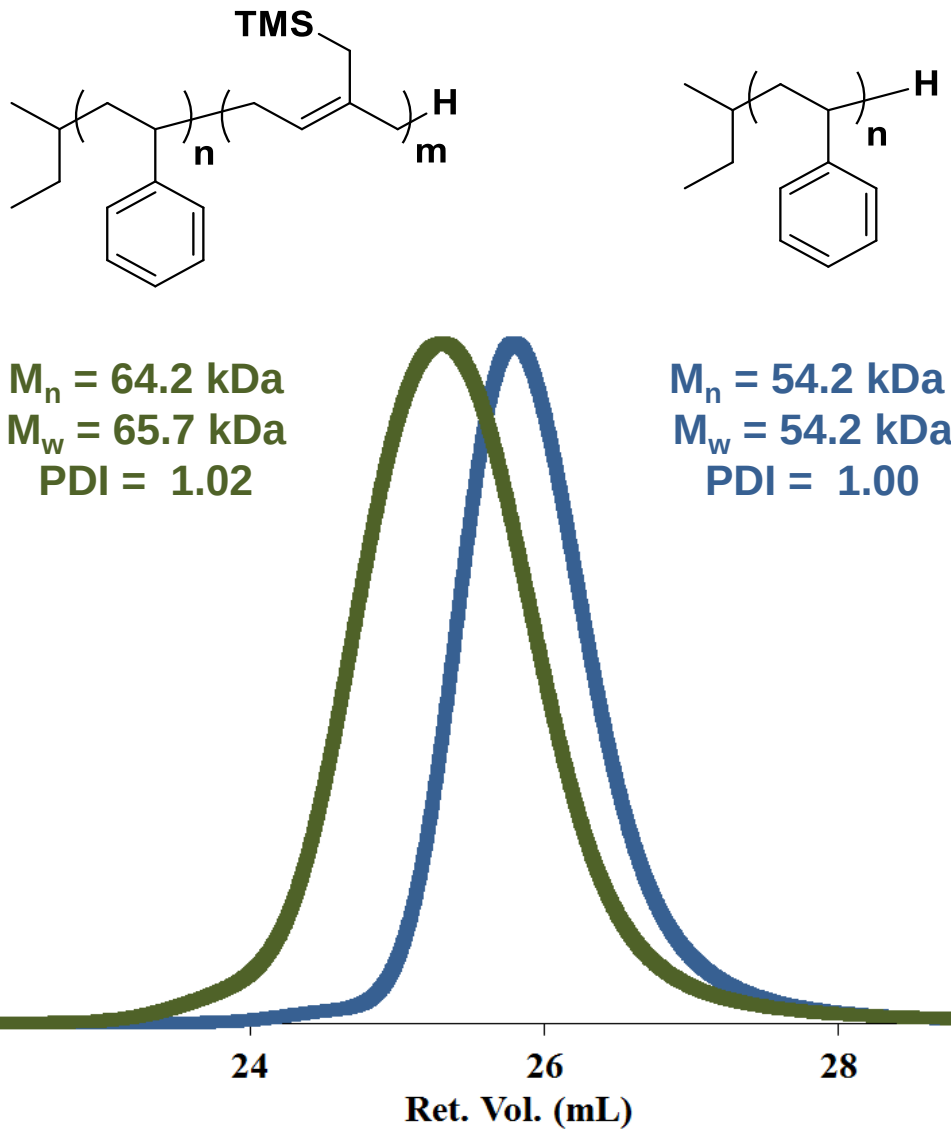
- Fast initiation
- Slower propagation
- No chain transfer
- No termination.



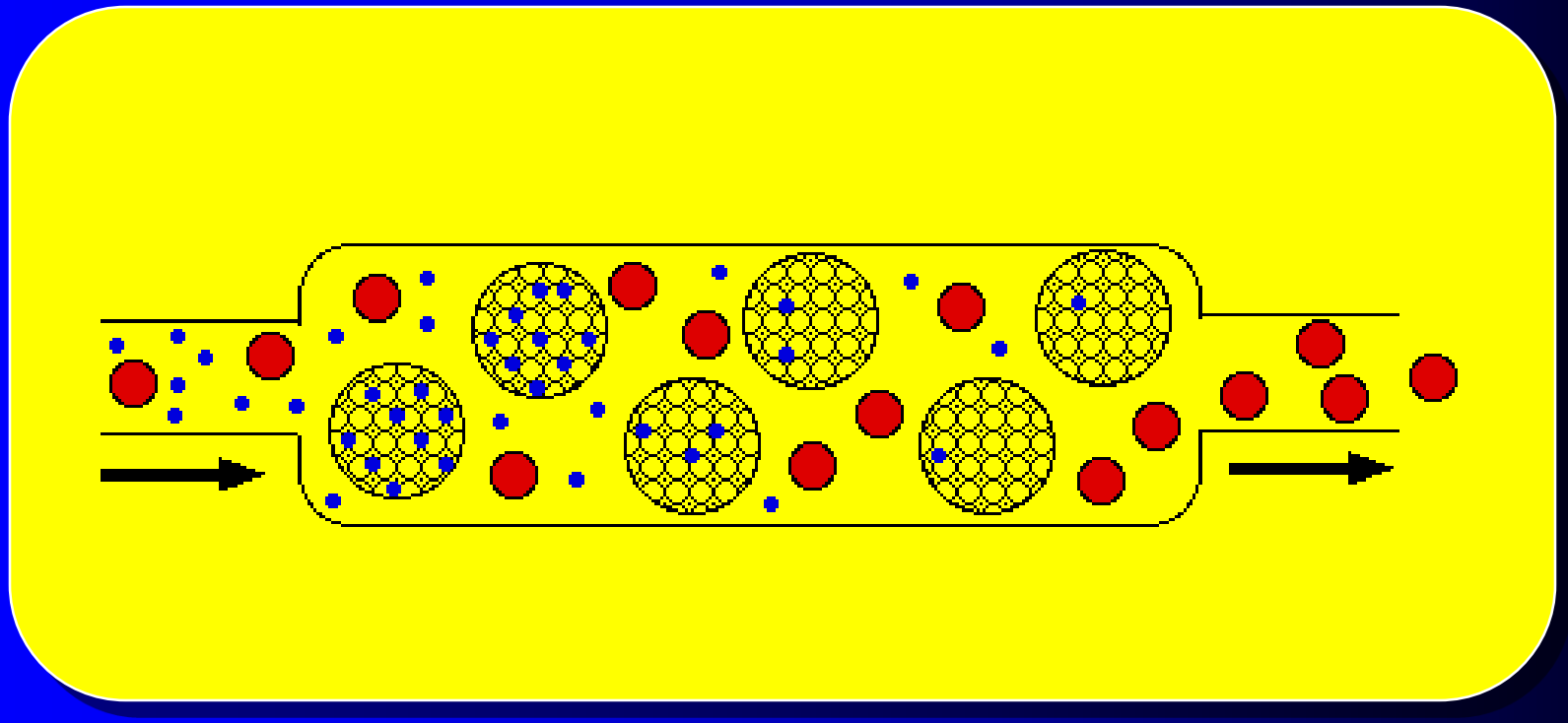
Miracle of Block Copolymers



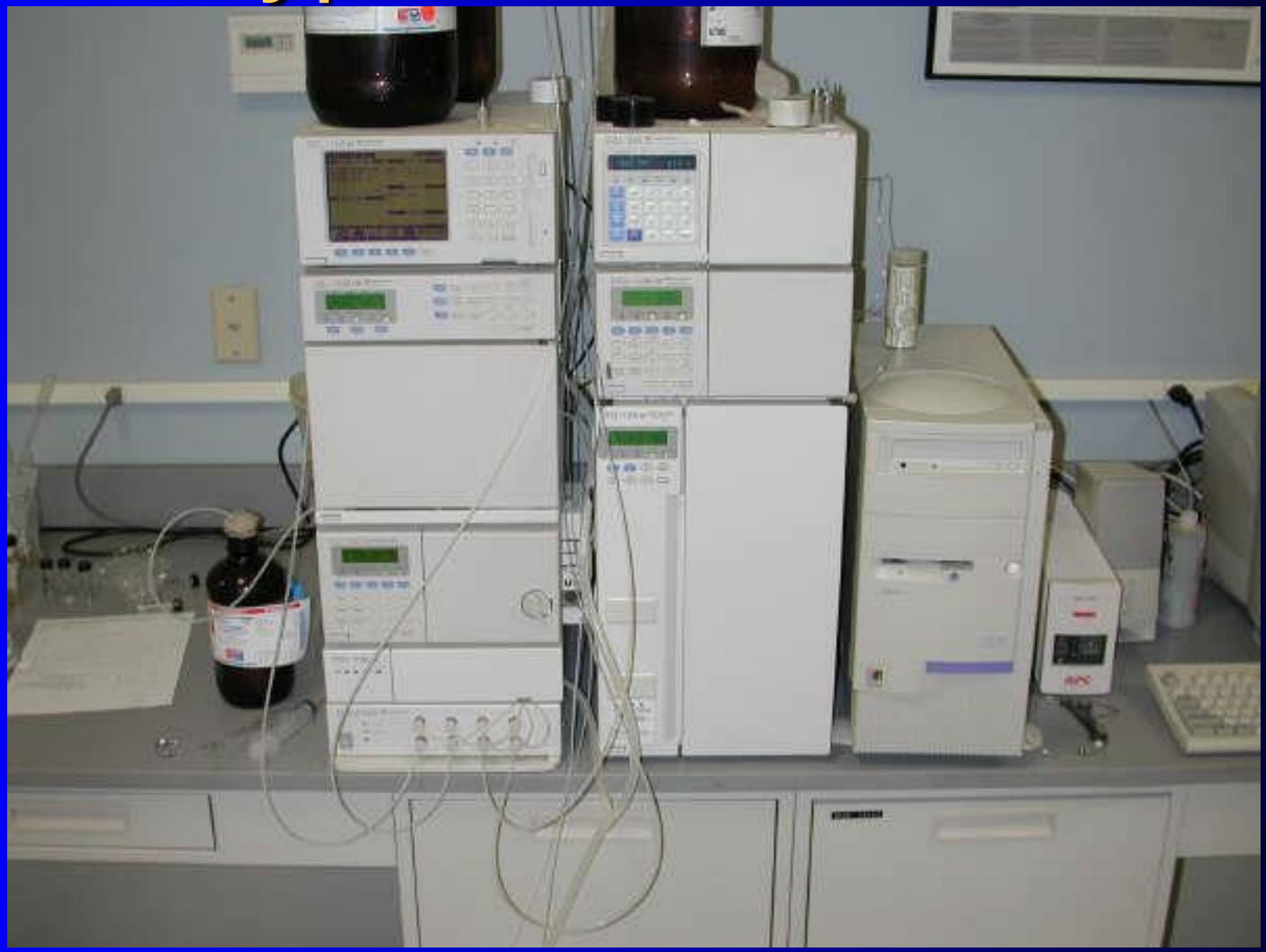
Anionic Polymerization of diblock copolymer



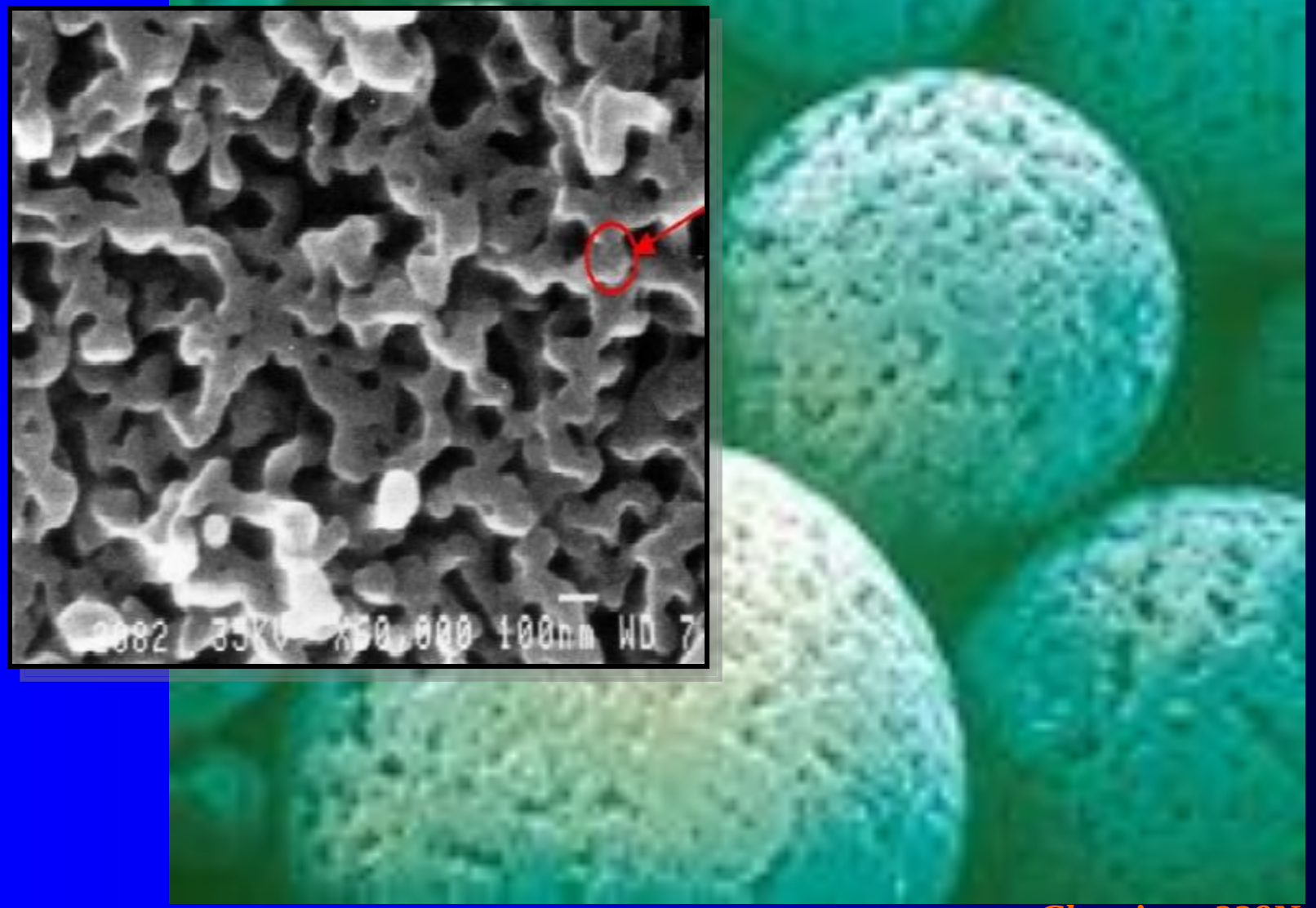
Size Exclusion Chromatography
Gel Permeation Chromatograpy



Typical Instrument



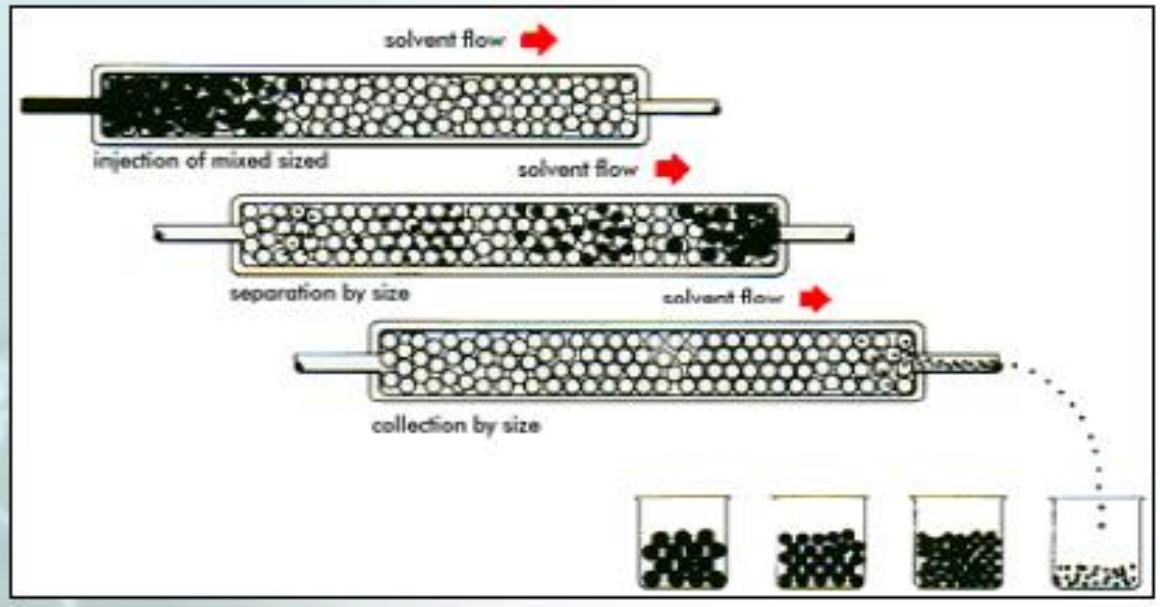
Size Exclusion Chromatography



SEC/GPC

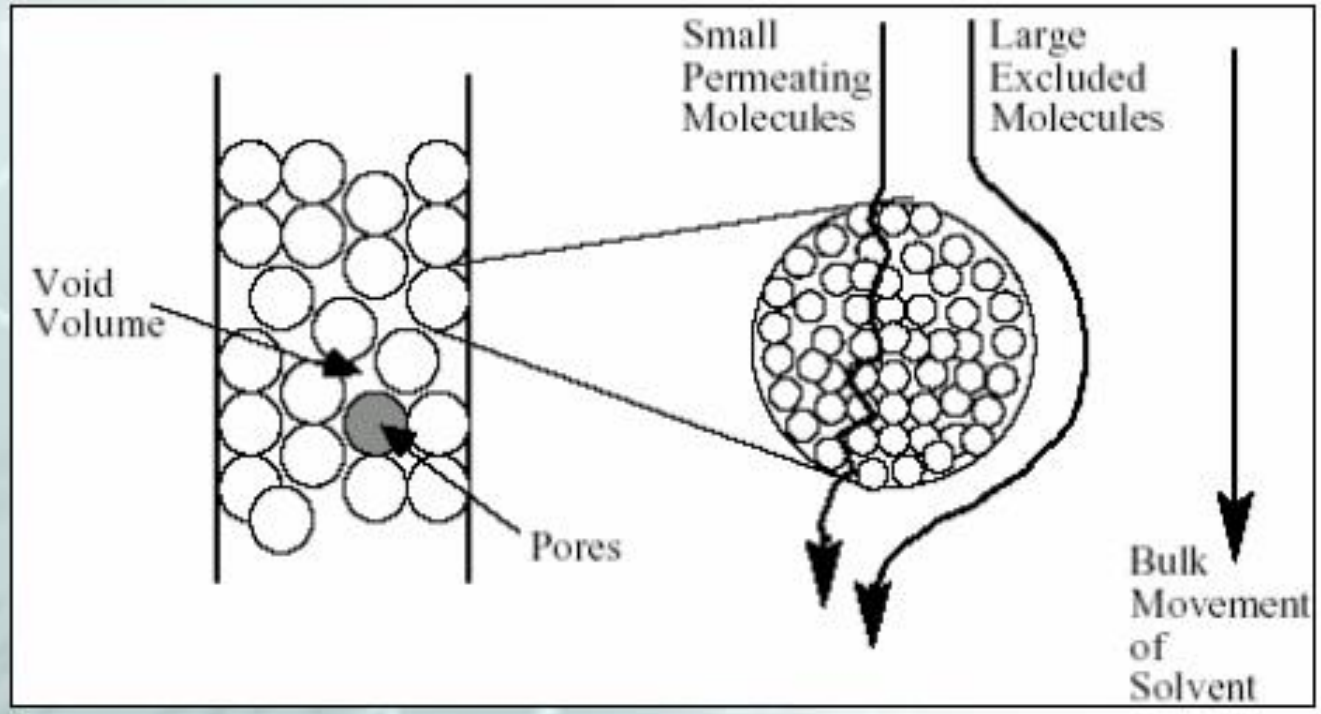
- ***Size Exclusion Chromatography*** (SEC), also known as ***Gel Permeation Chromatography*** (GPC) and ***Gel Filtration Chromatography*** (GFC) is the most widely used technique to determine the Molecular Weight Distribution of Polymers and Proteins.

- This technique employs a set of columns to separate the molecules based on their ***Hydrodynamic Size***.



SEC/GPC

✓ The exclusion process is carries out in columns employing ***porous packing material*** such as glass beads or polymer gels.



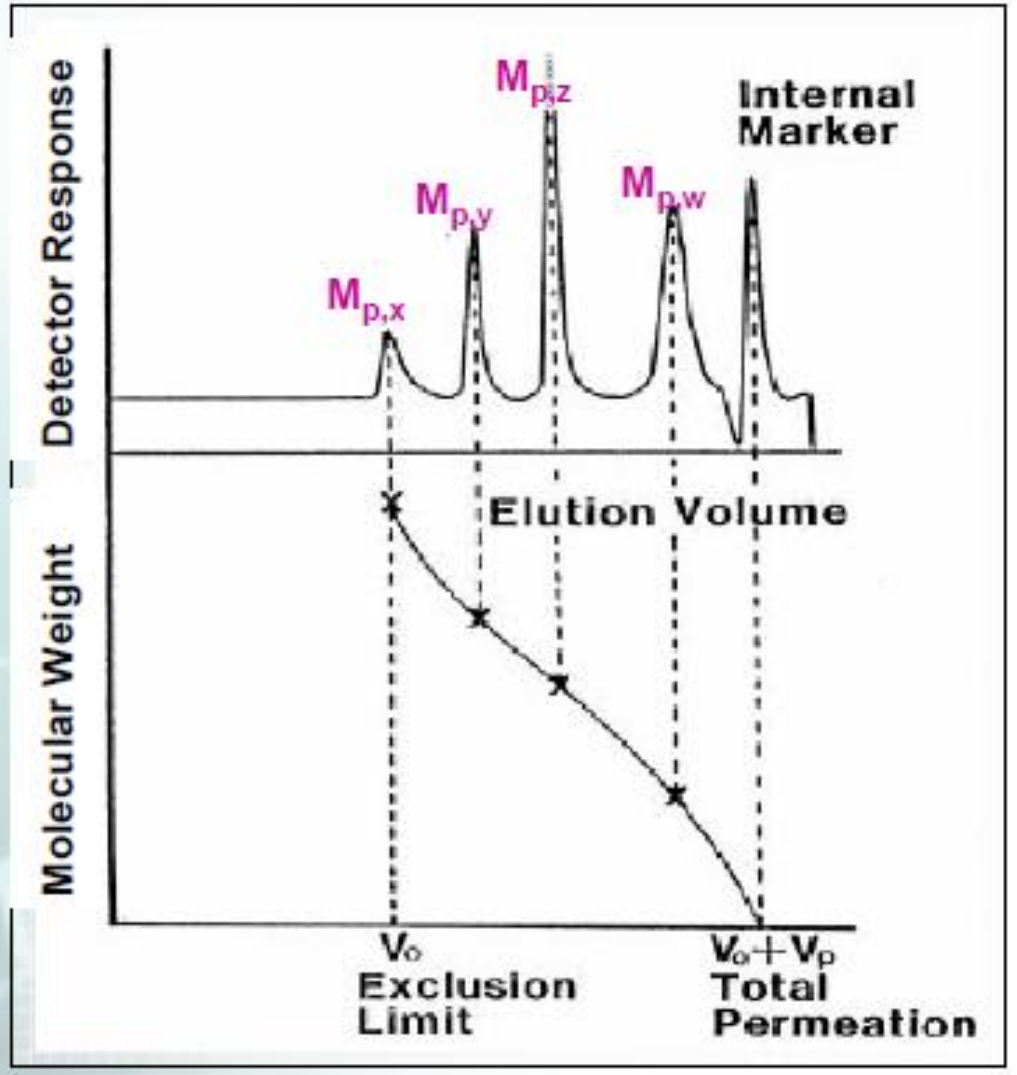
✓ Unlike HPLC, *no chemical interaction* occurs in the columns and the separation is solely based on molecular size.

Conventional Calibration

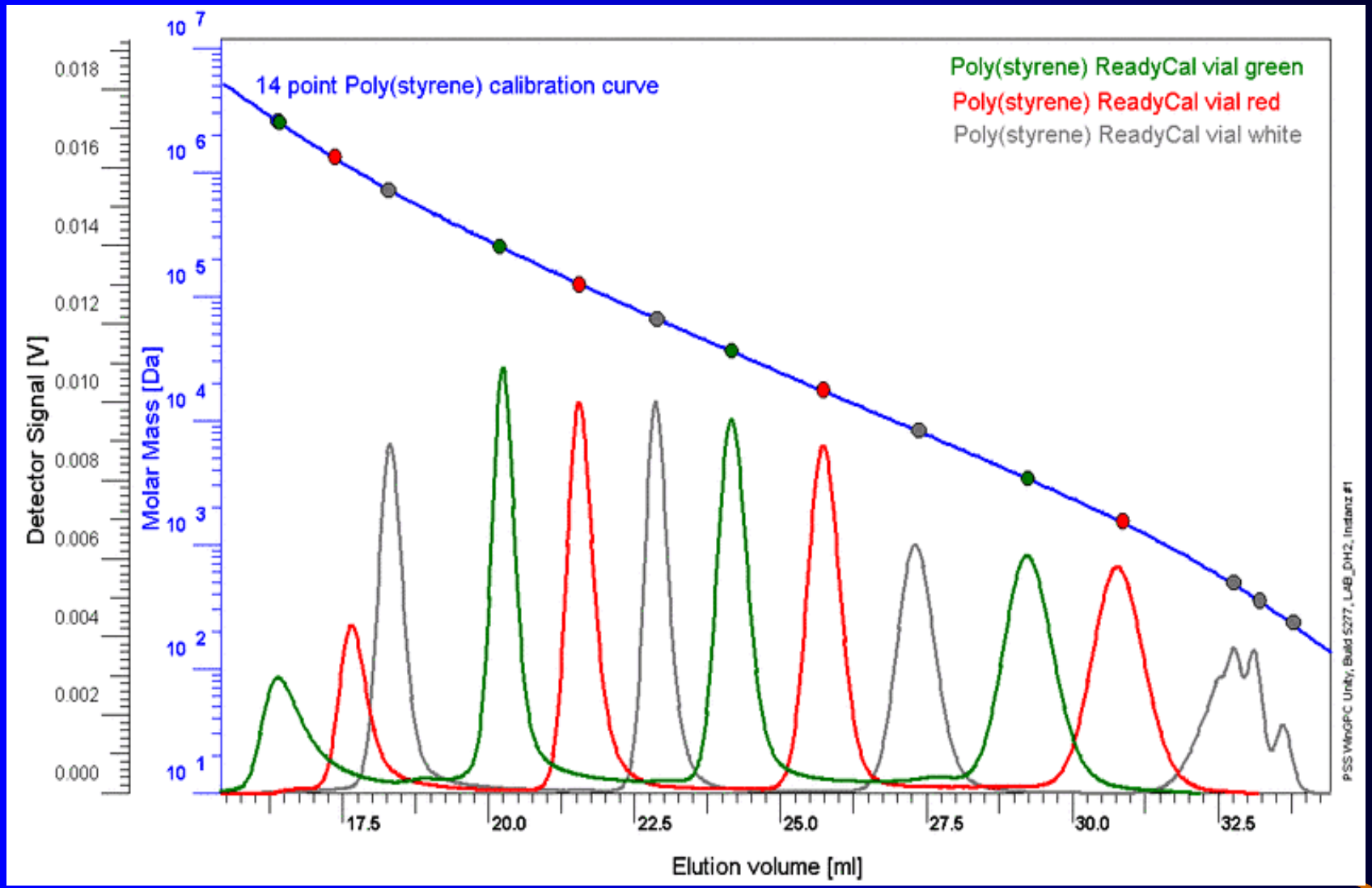
- Typically 12-15 narrow molecular weight standards is recommended to generate a calibration curve.

A mixed injection of standard "A" with the following molecular weight values:

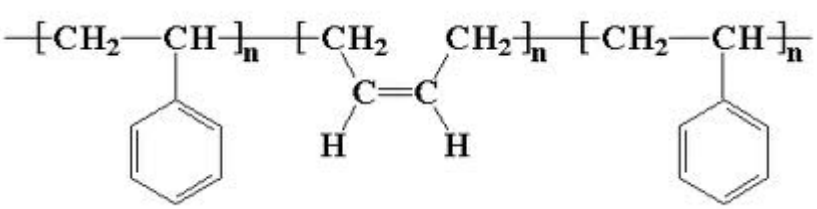
- ✓MW of x: $M_{p,x}$
- ✓MW of y: $M_{p,y}$
- ✓MW of z: $M_{p,z}$
- ✓MW of w: $M_{p,w}$
- ✓Internal Marker or Reference



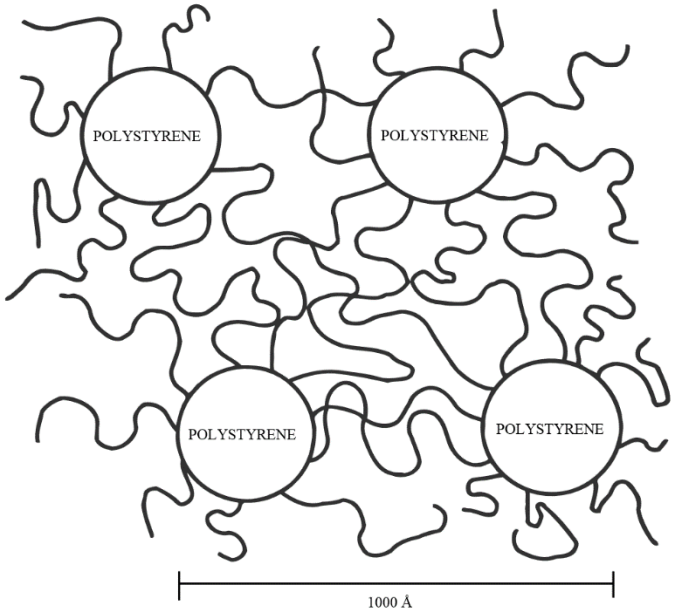
Calibration Run

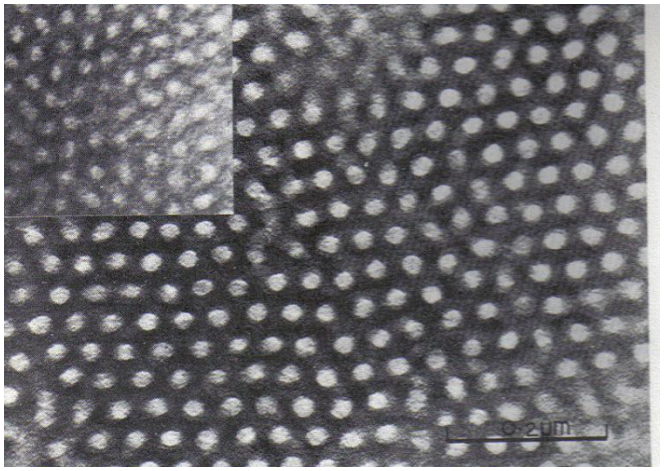


SBS Thermoplastic Elastomer

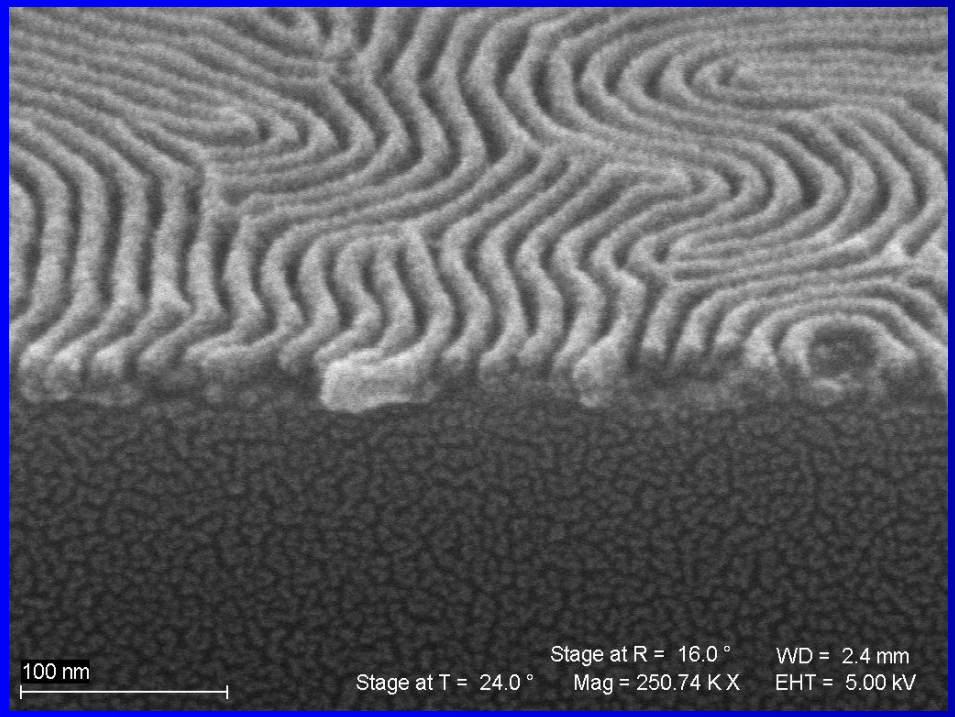


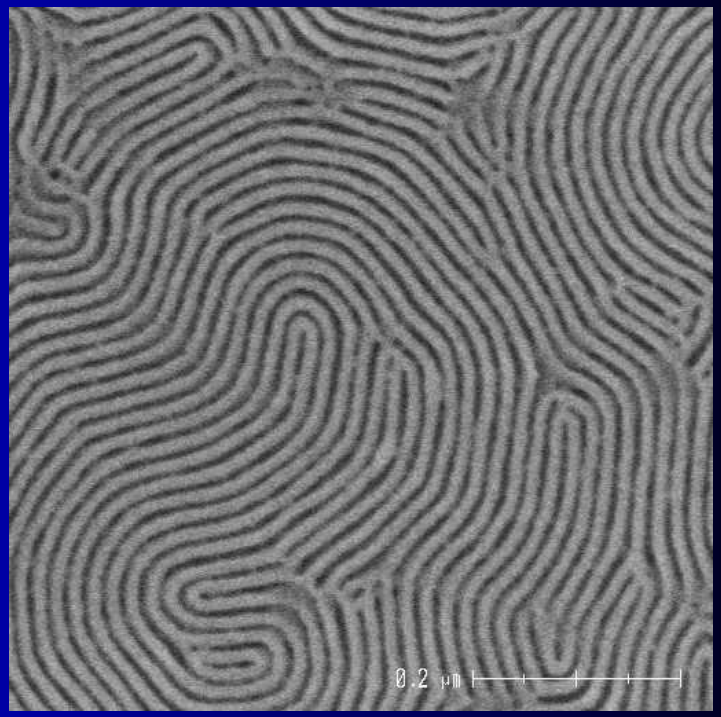
Krayton



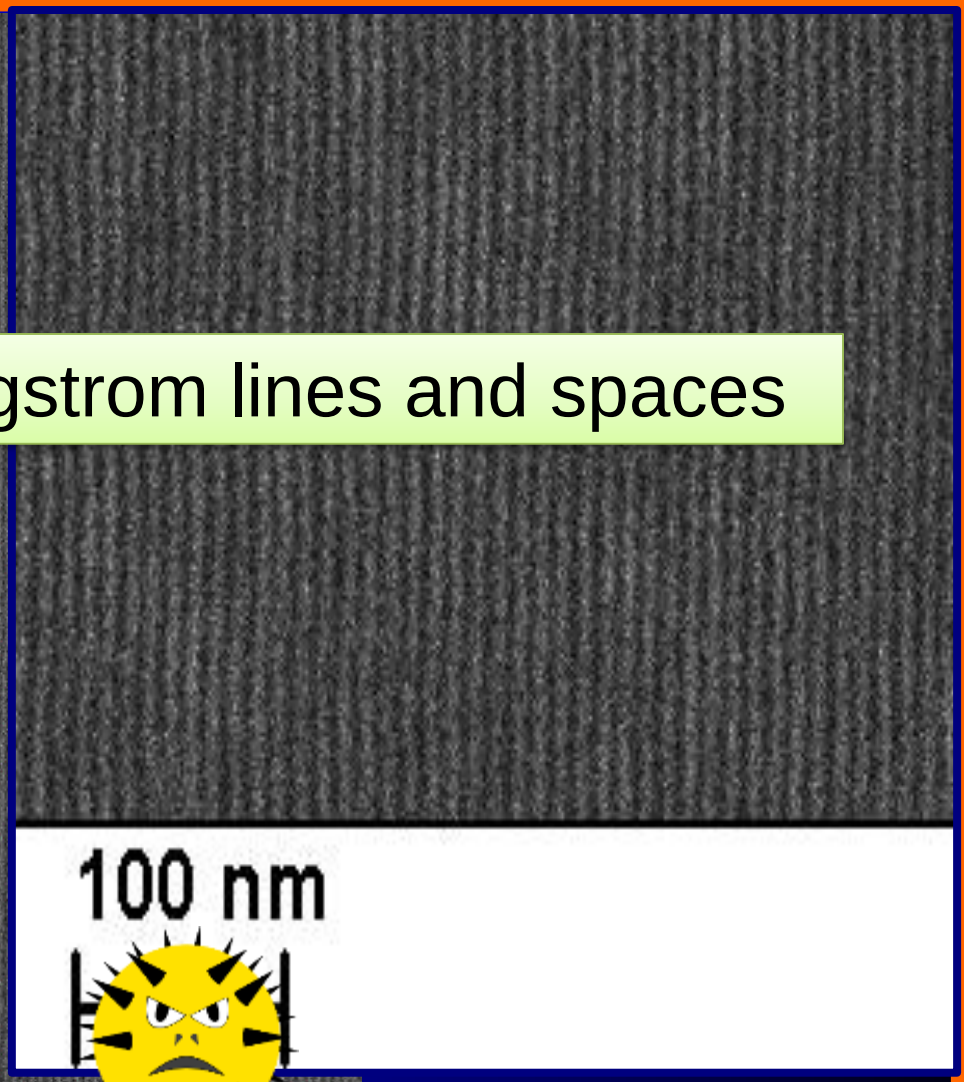


8nm lines in block copolymers





Etch developed 50 Angstrom lines and spaces



collaboration with

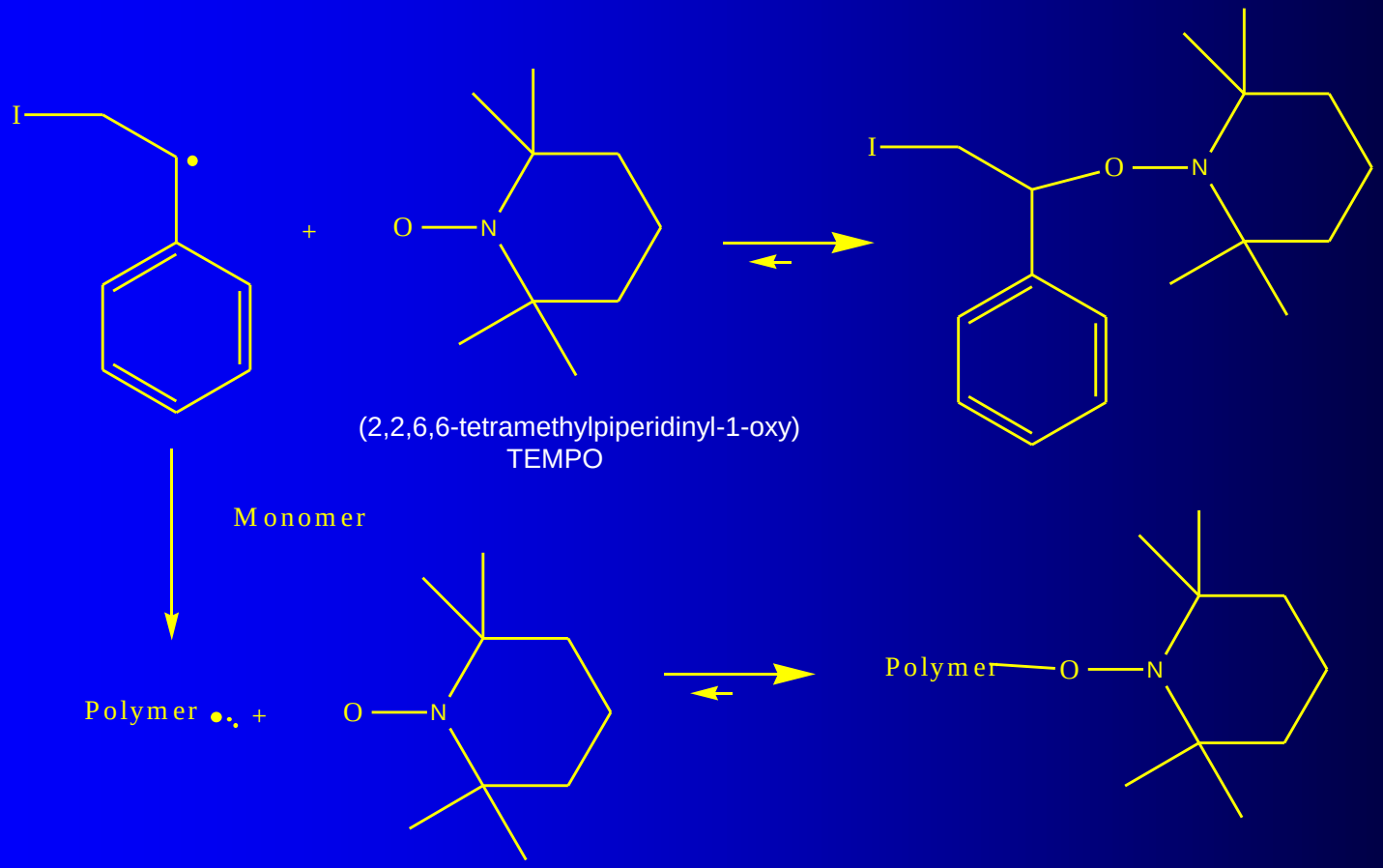
SEAGATE

Arthur K. Doolittle Award

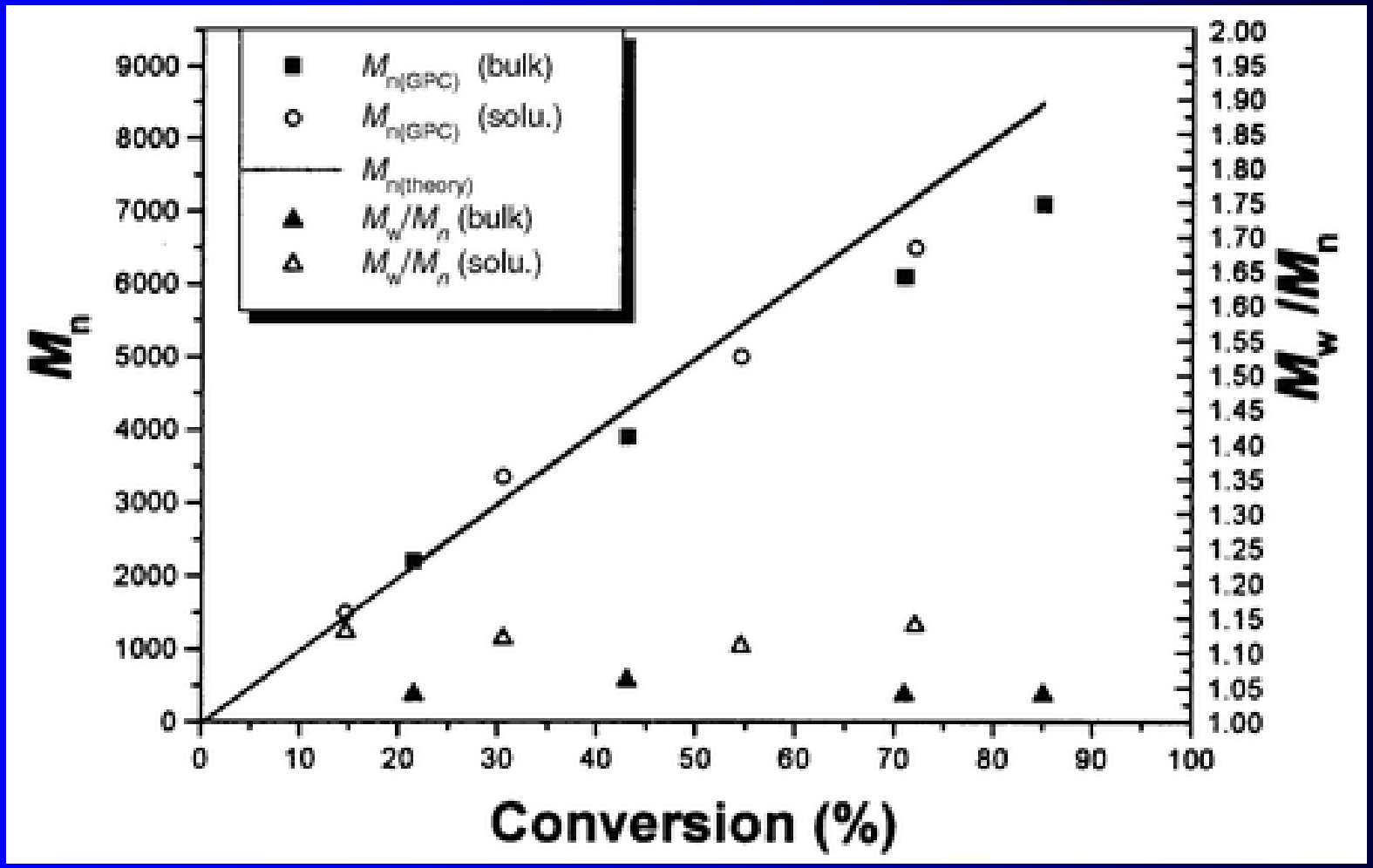
The Arthur K. Doolittle Award, established by the Union Carbide Corporation, is given to the authors of an outstanding paper presented before the PMSE Division at each national meeting of the ACS. A prize in the amount of $1,000.00 is financed with the gift of royalties from A. K. Doolittle's book, *Technology of Solvents and Plasticizers*. All papers are evaluated on the basis of content, with emphasis on originality and development of new concepts, and on the quality of presentation. Recipients are selected by an anonymous panel of judges appointed by the Chairman of the Doolittle Award Committee.

TEMPO Controlled Polymerization

1993 M. K. Georges, R. P. N. Veregin, P. M. Kazmaier and G. K. Hamer (Xerox Corporation), "Narrow Molecular Weight Resin by Free Radical Process."

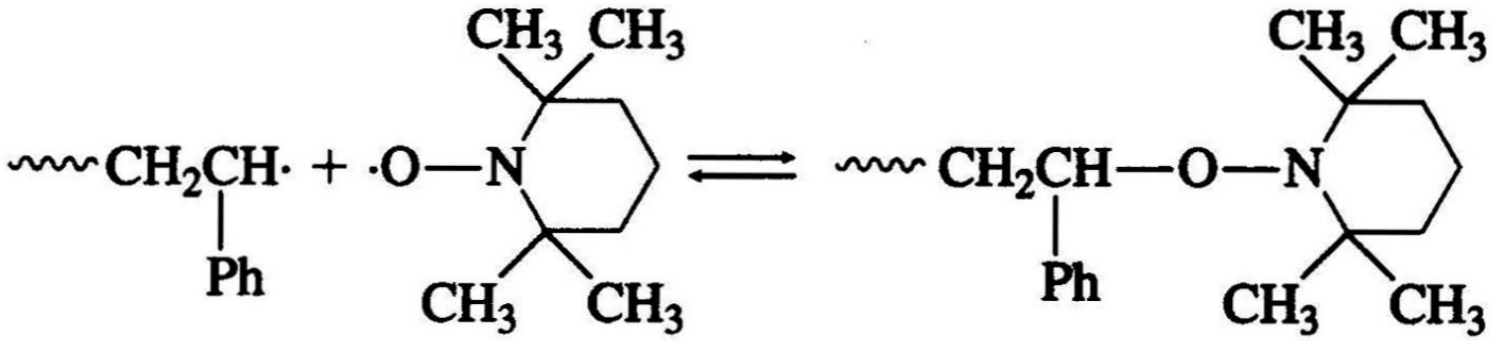


Controlled Free Radical Polymerization



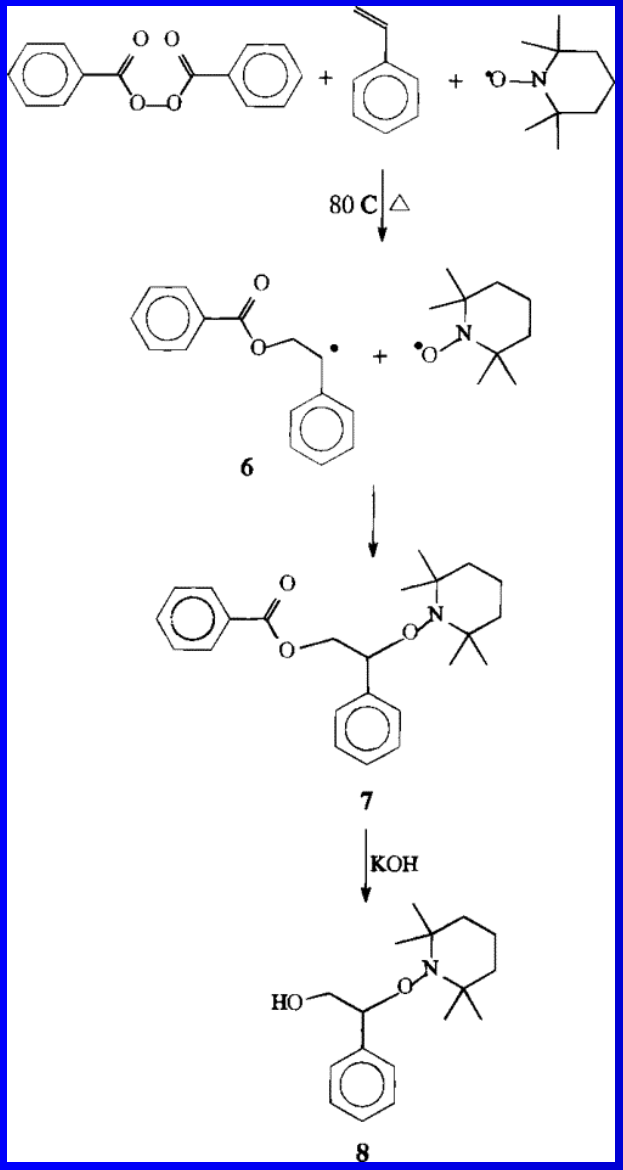
Living Radical Polymerization

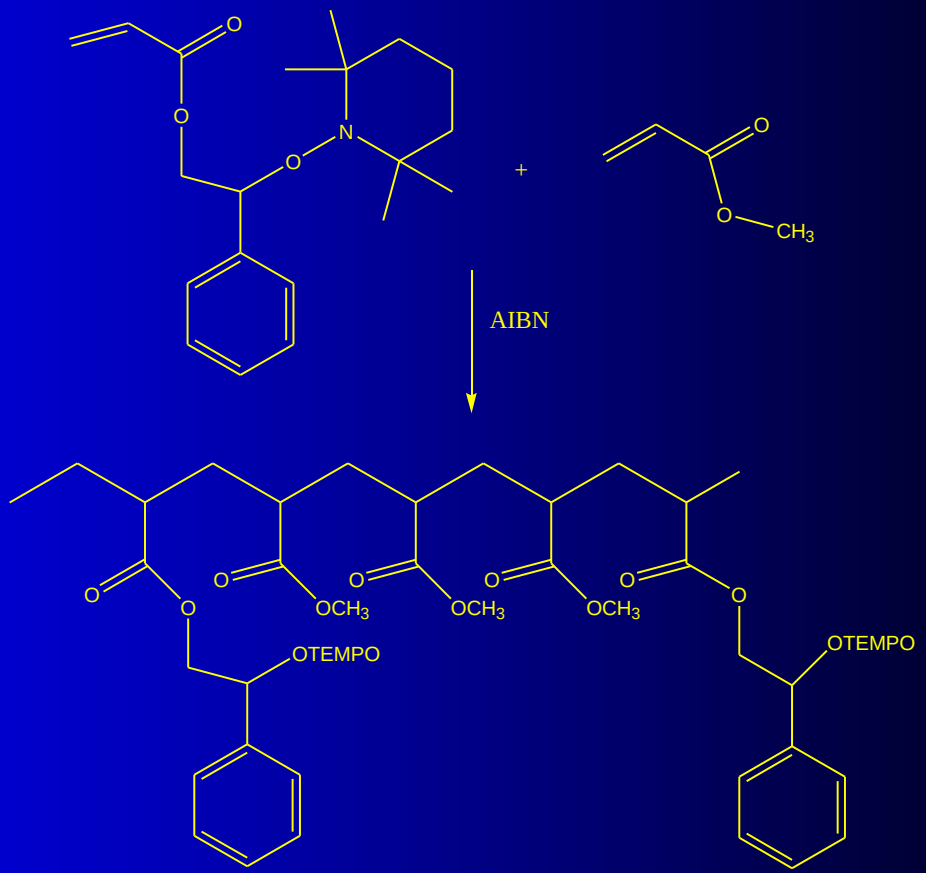
- Polymerize styrene with benzoyl peroxide plus TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy)
- TEMPO is too stable to initiate the polymerization
- TEMPO combines reversibly with chain ends, keeping them alive

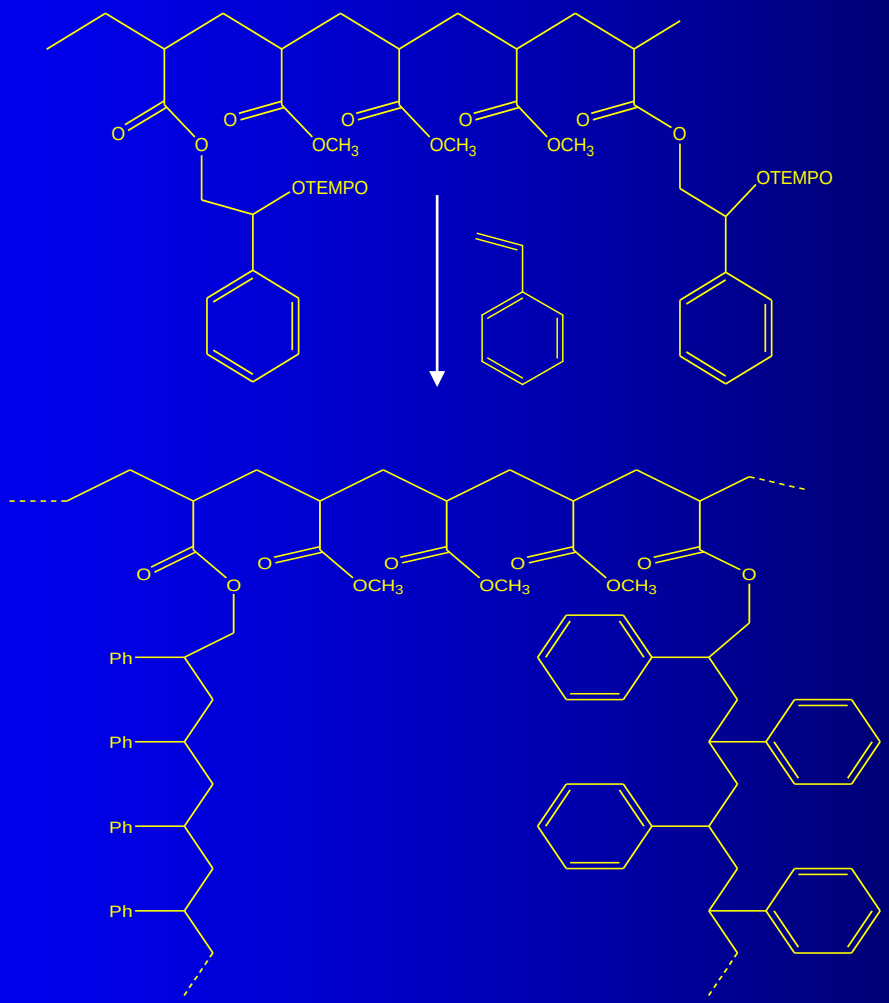


TEMPO

Control of polymer Architecture

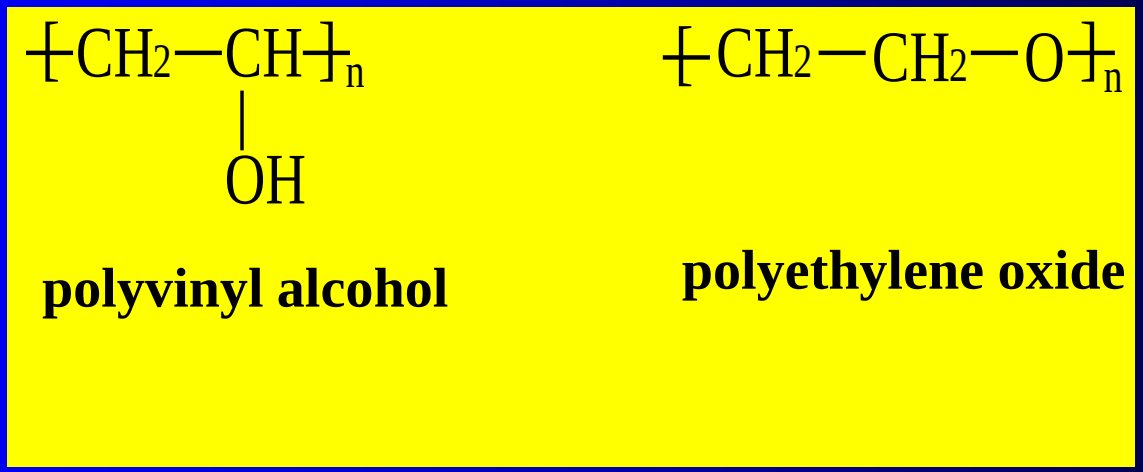




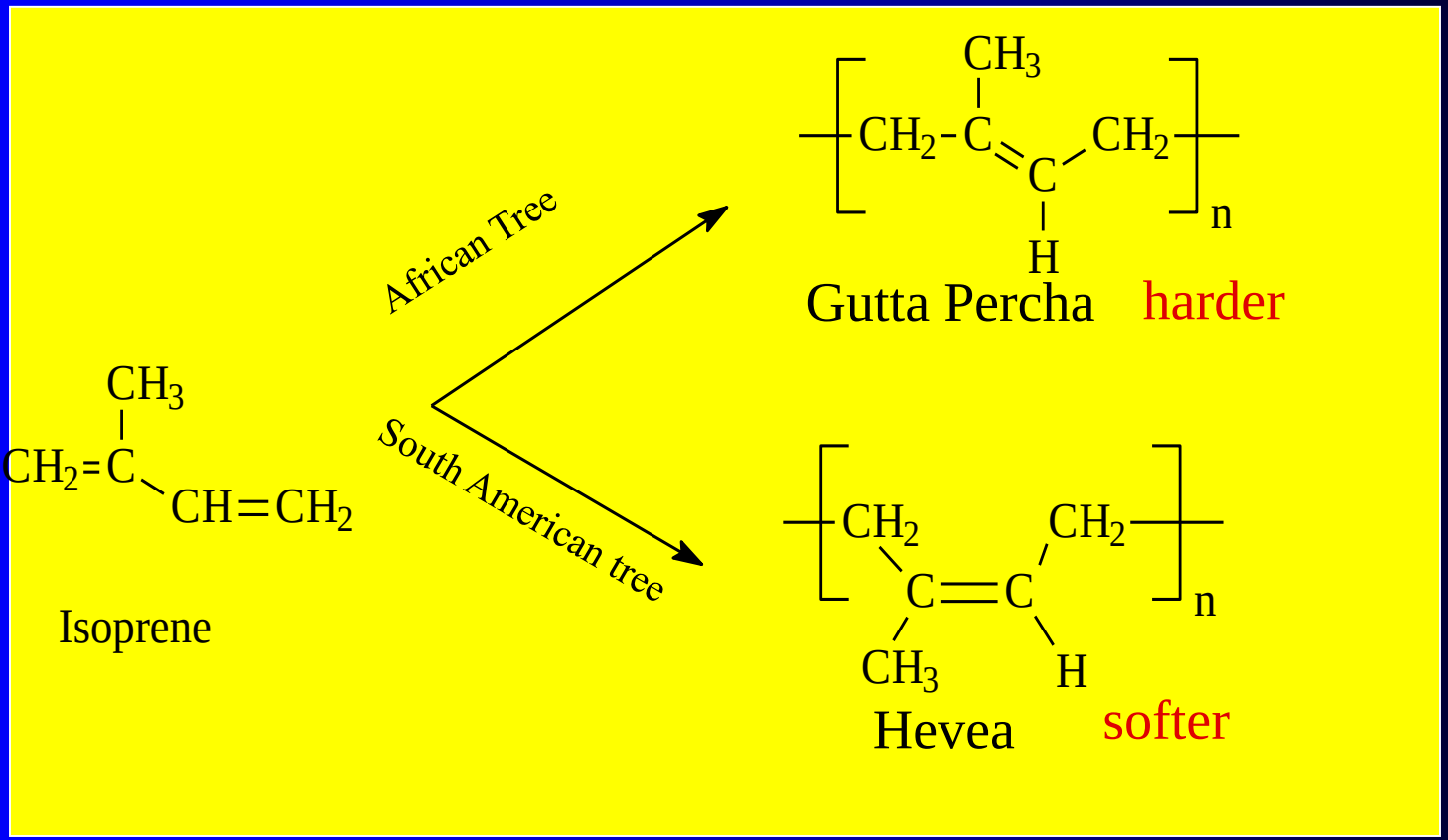

O
OCH3
OTEMPO
Ph

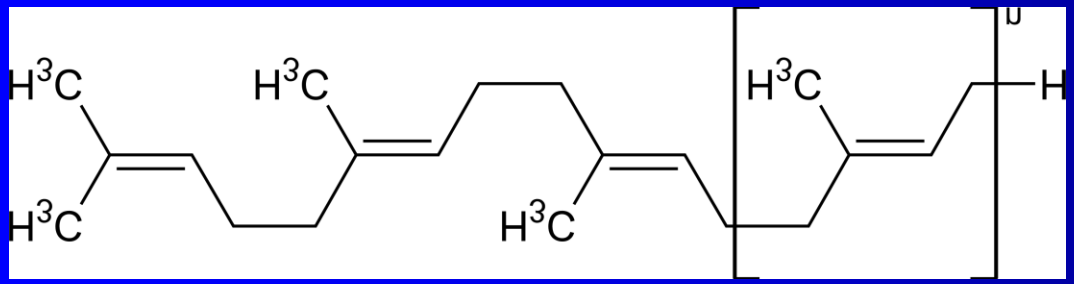
Isomers of Polymers

- For example , polymer with structure unit $-[C_2H_4O-]_n$ can be polyvinyl alcohol or polyethylene oxide

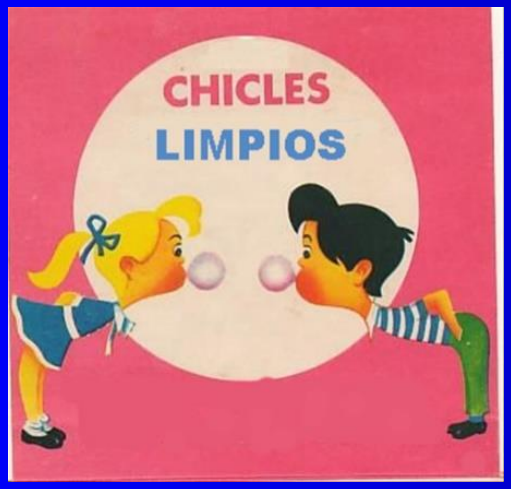


Natural Rubber (isomers matter)

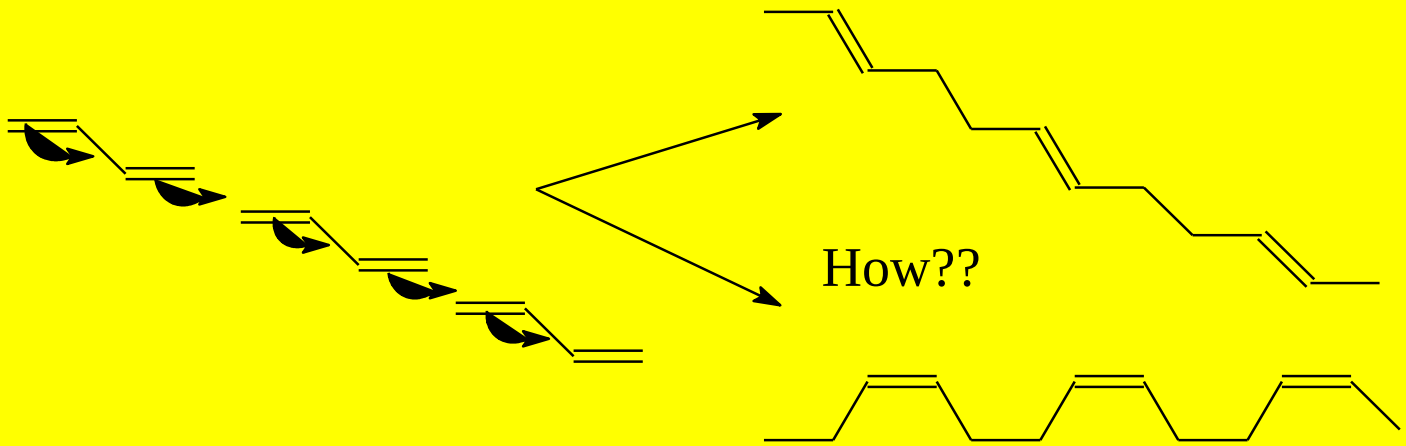




Chicle (**Manilkara zapota**), native tree of Central America and the West Indies.

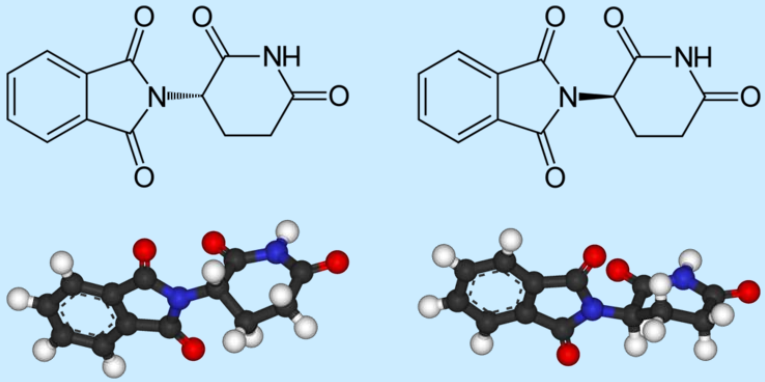


The synthetic rubber program



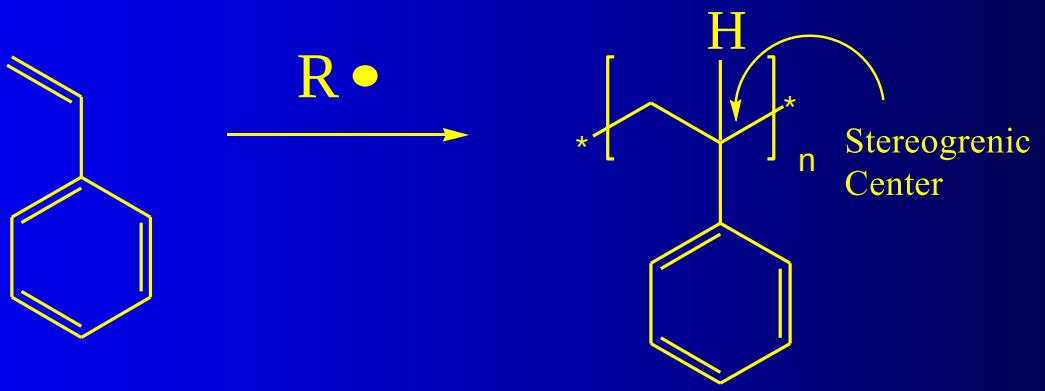
See web links for more history

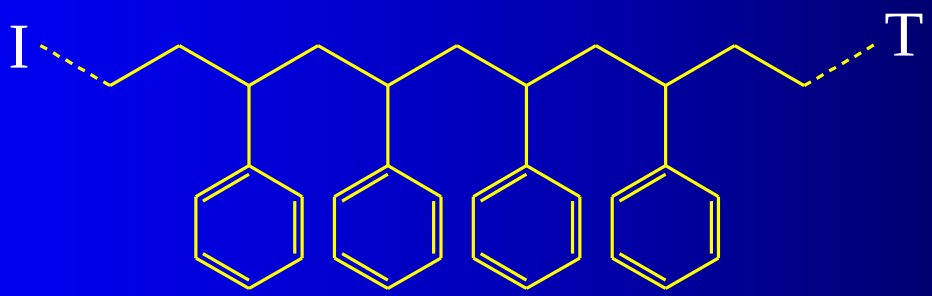
Stereochemistry Matters!

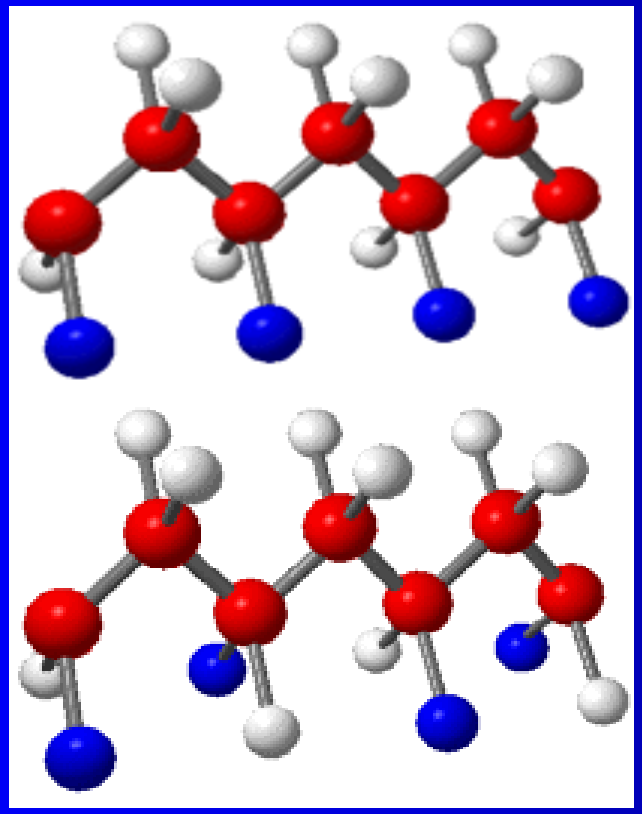


Thalidomide

Polystyrene



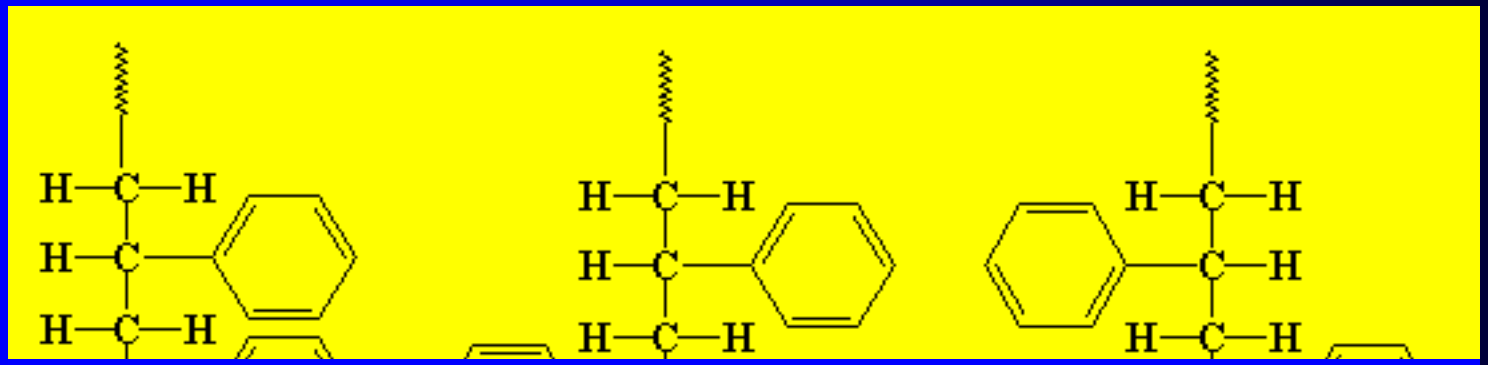




Isotactic

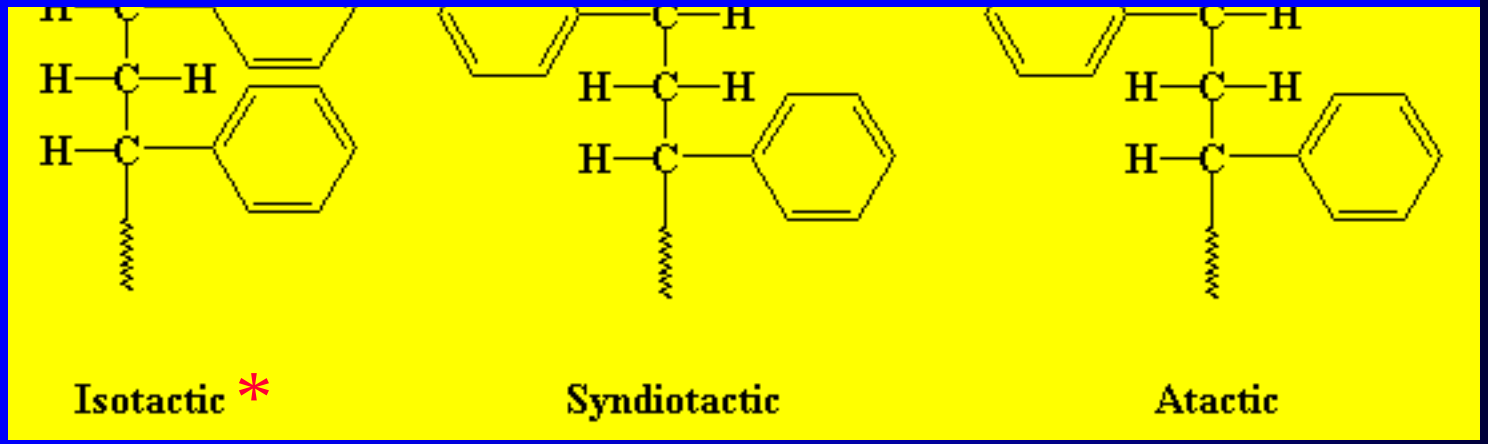
Syndiotactic

Tacticity in Polystyrene



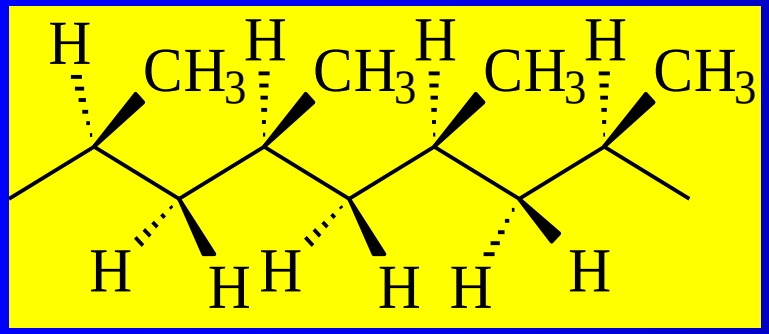
?????? Tm = 270 °C Tg = 100 °C

Tacticity Matters

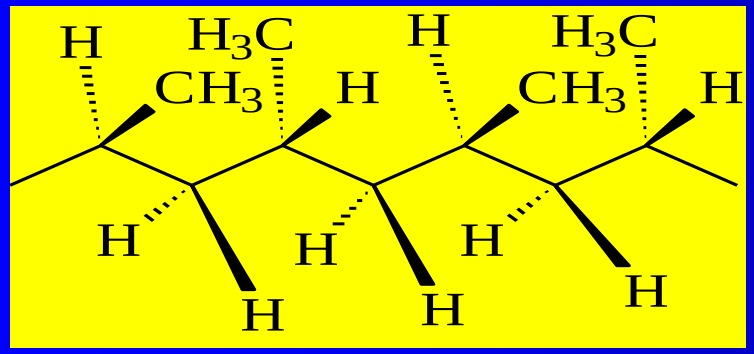


* For you to figure out how to make!!

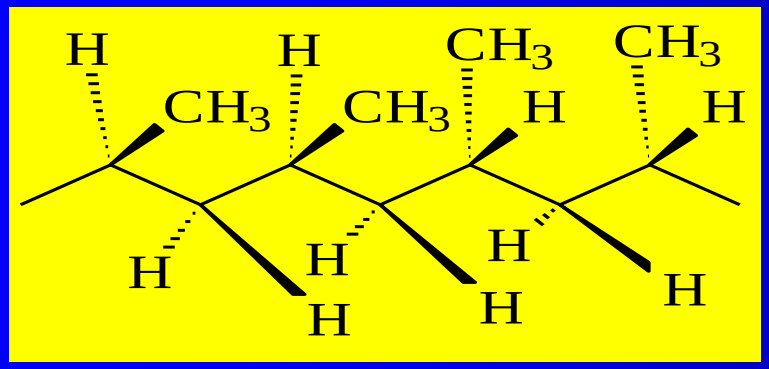
Polypropylene



Isotactic 160-170 ^{0}C



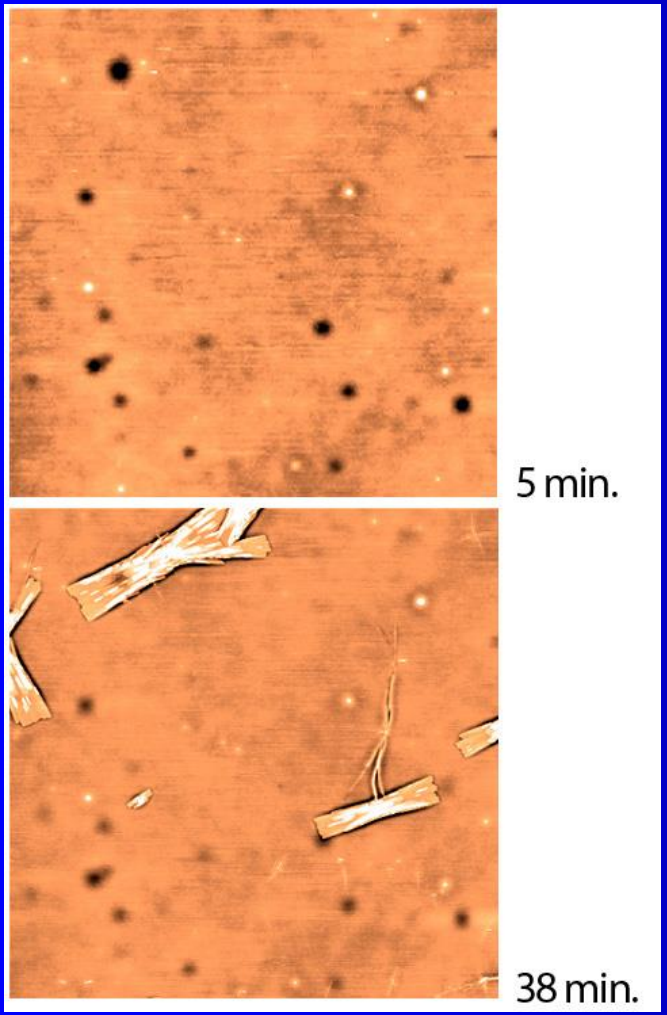
Syndiotactic 125-131 ^{0}C

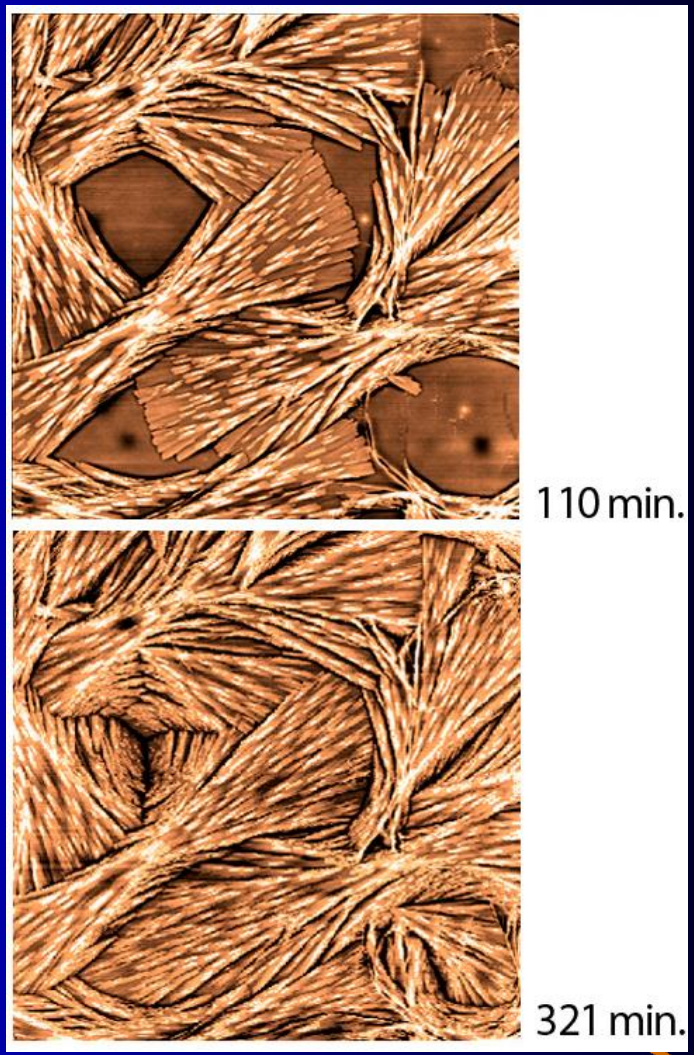


Atactic 0 ^{0}C

Syndiotactic polypropylene

Melted at 160°C and cooled to 105°C





Hogan and Banks

Phillips Petroleum

J. Paul Hogan

Robert L. Banks

Inventors of Crystalline Polypropylene and High Density Polyethylene.

Hogan and Banks, of Phillips, were granted a patent on crystalline polypropylene on March 15, 1983—more than thirty years after their discovery.

Crystalline PE and PP

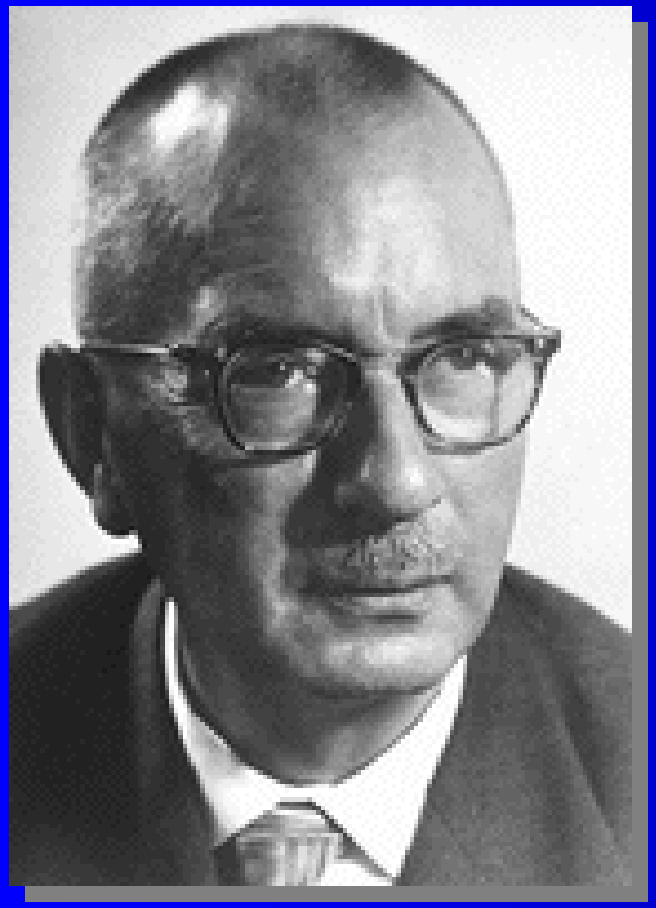
A low cost, high melting thermoplastic

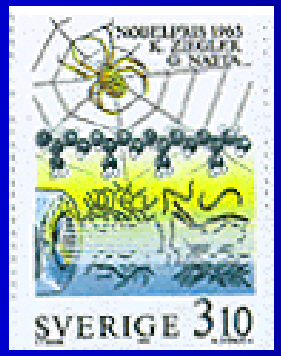
“Saving Phillps”

Over 100 million sold in 1958!!

Hula Hoop

Karl Ziegler and Guilio Natta

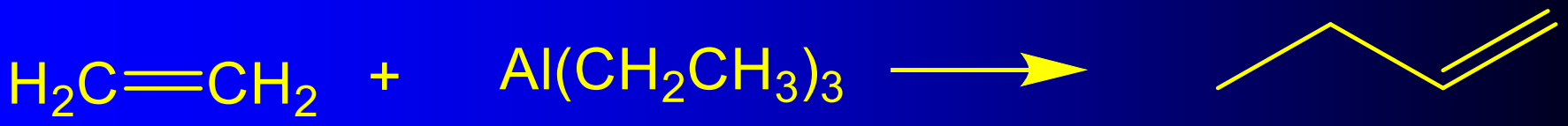




- Nobel Prize in Chemistry 1963

A Quick History

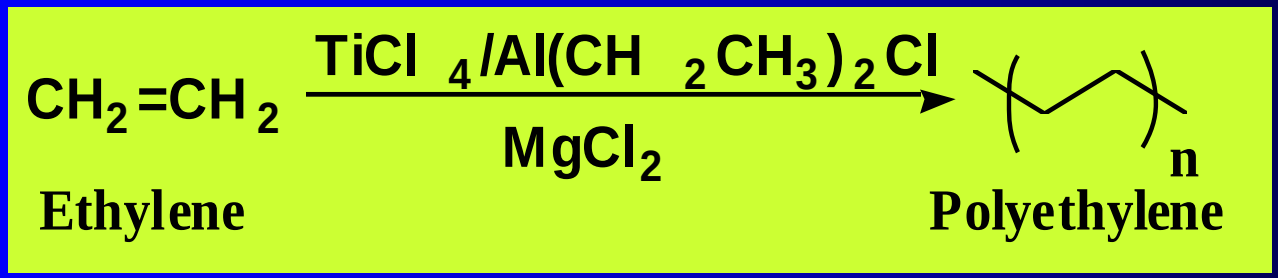
- 1949 Ziegler and Gellert find 1-butene from ethylene in contact with ethyl aluminum



- Led to studies with LiH but it was too stable
- Tried $LiAlH_4$,,,which worked "Nicely"
- 1952 Hozkamp studies ethyl aluminum and ethylene at high pressure and temperature in metal cylinders…Cr gave some polymer……Zirconium gave a lot of polymer
- Indictment of metal led to systematic testing of elements and the "es geht in Glass" response for titanium from Martin.

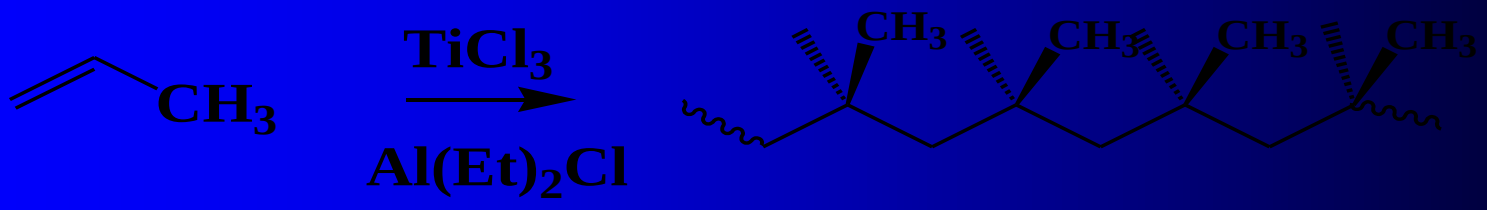
Ziegler-Natta Polymers

- Ziegler-Natta chain-growth polymerization does not involve radicals
  - Ziegler-Natta catalysts are heterogeneous materials composed of a $MgCl_2$ support, a group IVB transition metal halide such as $TiCl_4$, and an alkylaluminum compound

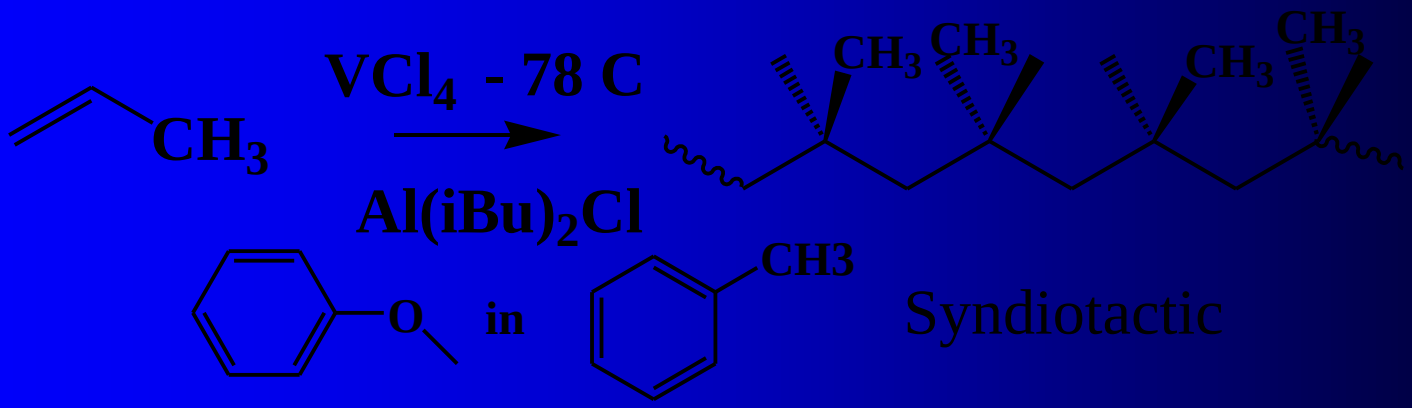


Natta's Discovery

- **1954 Guilio Natta, P. Pino, P. Corradini, and F. Danusso**
- J. Am. Chem. Soc. 77, 1708 (1955) Crystallographic Data on PP
- J. Polym. Sci. 16, 143 (1955) Polymerization described in French



Isotactic



Syndiotactic

Ziegler and Natta awarded Nobel Prize in 1963

Advantages of Ziegler Natta Catalysts

Before:

- Polyethylene was a highly branched polymer called high pressure polyethylene (because of high pressures used in its preparation)
- These high pressures made the polymer very expensive to produce and this reduced its commercial viability.

Now:

- With Ziegler-Natta catalysts the polymer is produced at much lower pressures and it is a much less branched polymer than its predecessor.
- Polymers produced with Ziegler-Natta catalysts have higher melting points which makes them much more commercially viable than the previous high pressure polymers.

Litigation

Polypropylene: Isotactic discovered by G. Natta in 1953 (Milan)

Company: Montedison (La Montecatini Edison)

Montecattini

Montell

Bassell (2000 – BASF/Shell)

vs.

Phillips Petroleum (Bartlesvill

Du Pont

Union Carbide

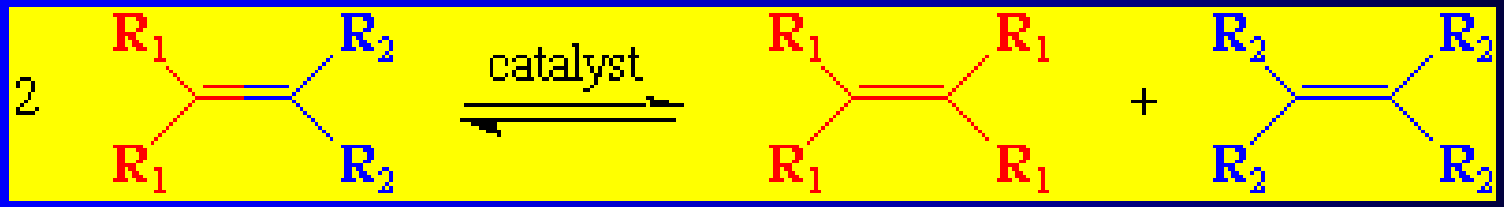
Harry J. Rober

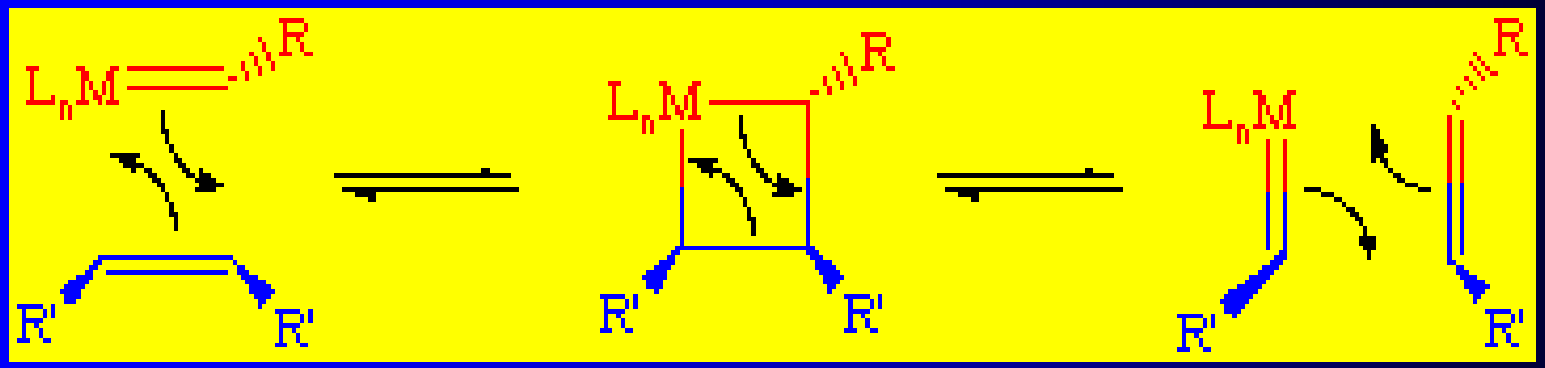
Litigation started 1953-ended in 1983

Magic Metals!

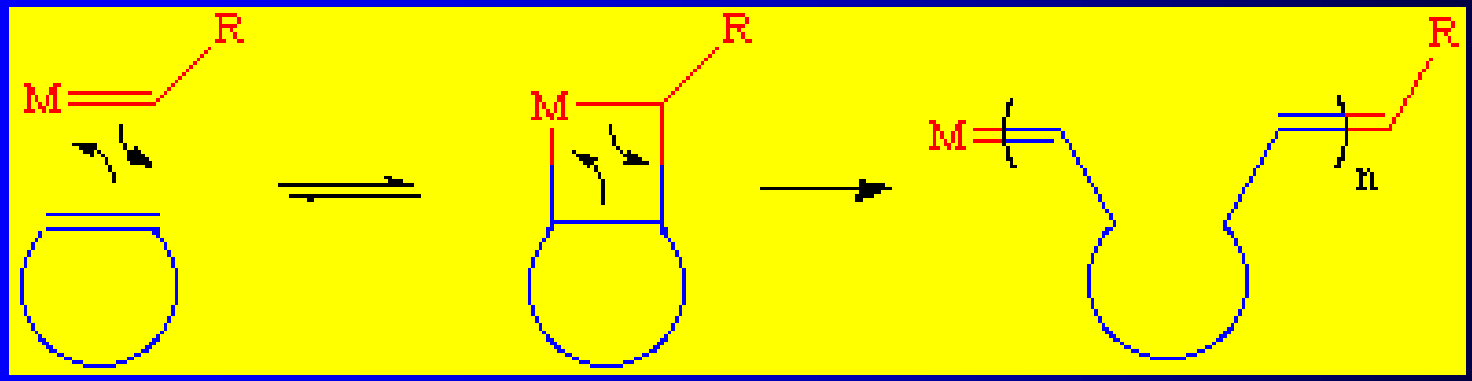
- Led to production of Cis-polybutadiene rubber
- High density polyethylene (no branches)
- Isotactic and syndiotactic polypropylene
- Multiple other commercial polymers
- Still an active field of research
- 2005 Nobel Prize for Metal catalysts

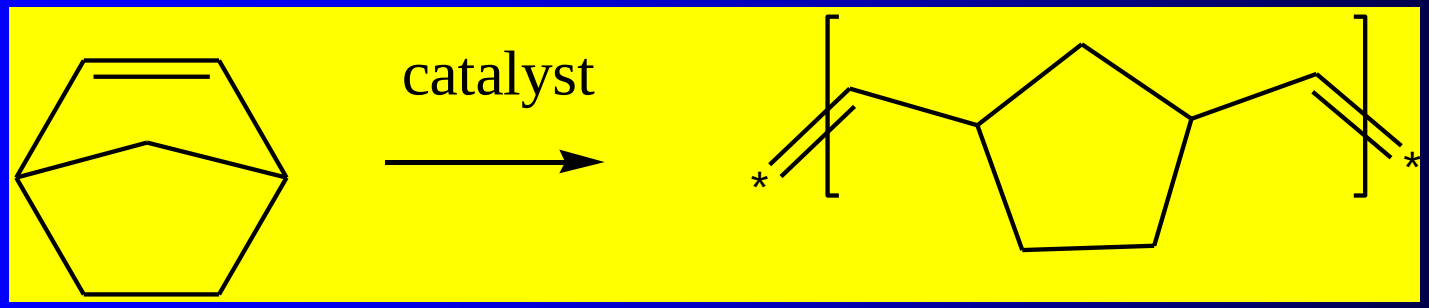
Olefin Metathesis



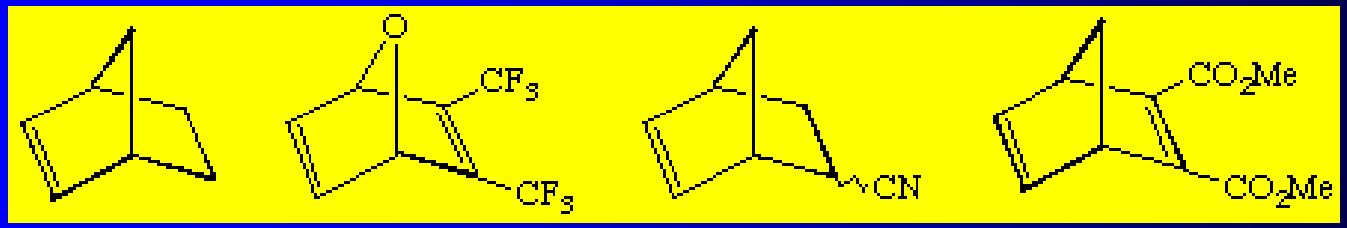


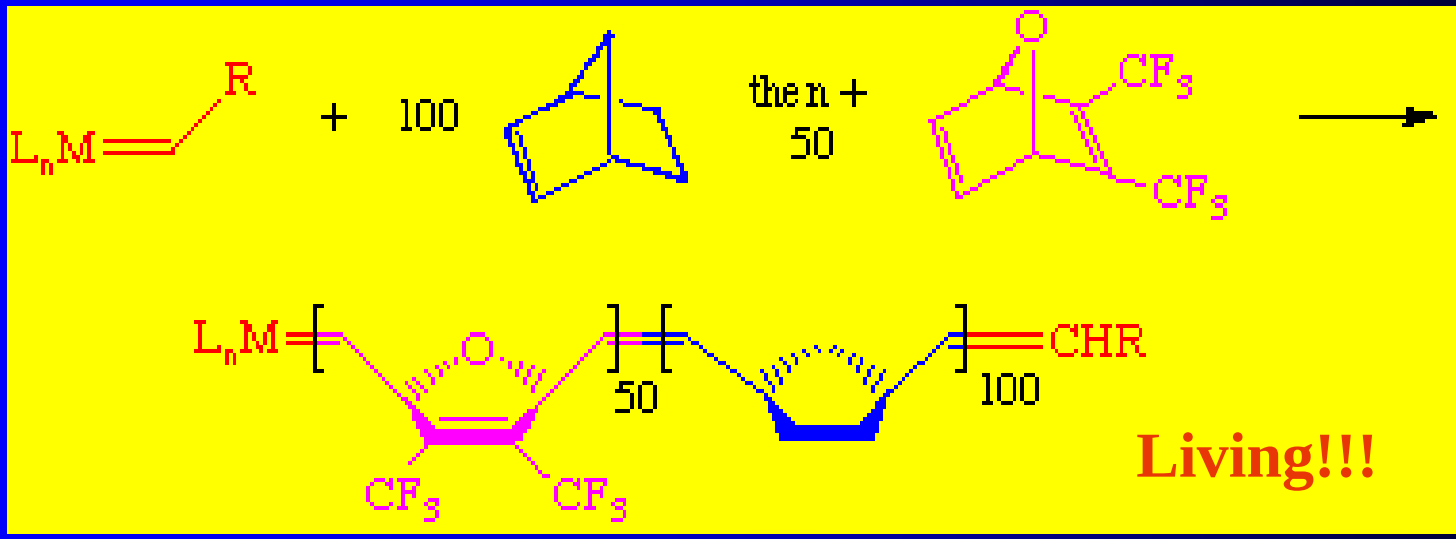
Ring opening metathesis polymerization ROMP





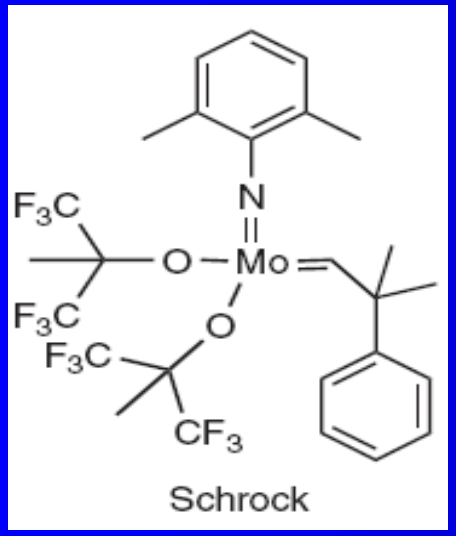
Ring strain driving force



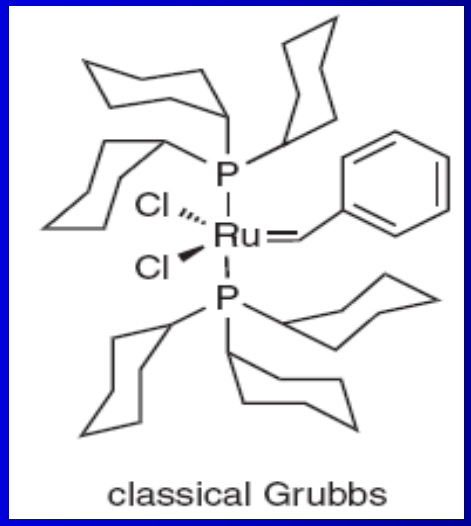


Olefin Metathesis Catalysts

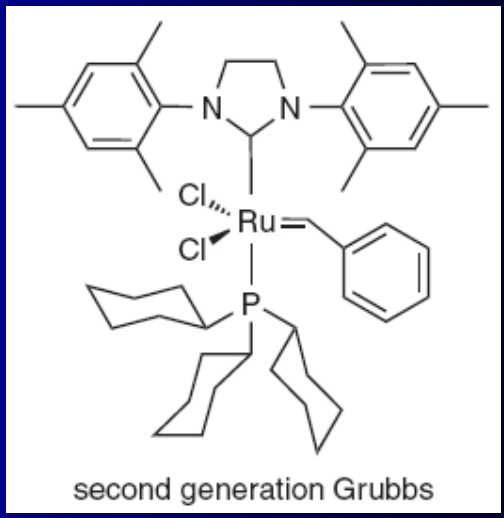
- Schrock and Grubbs
  - Schrock's were Air sensitive
  - Schrock molybdenum and Grubbs ruthenium based
  - Shared 2005 Nobel Prize with Chauvin



Schrock



classical Grubbs



second generation Grubbs

Images from Pappenfus, T. M. Synthesis and Catalytic Activity of Ruthenium-Indenylidene Complexes for Olefin Metathesis, *J. Chem. Ed.* **2007,** 84 (12), 1998-2000.

2005 Nobel prize in chemistry

"for the development of the metathesis method in organic synthesis"

Yves Chauvin
Institut Français du Pétrole
Rueil-Malmaison, France b

Robert Grubbs
California Institute of Technology
(Caltech) Pasadena, CA, USA

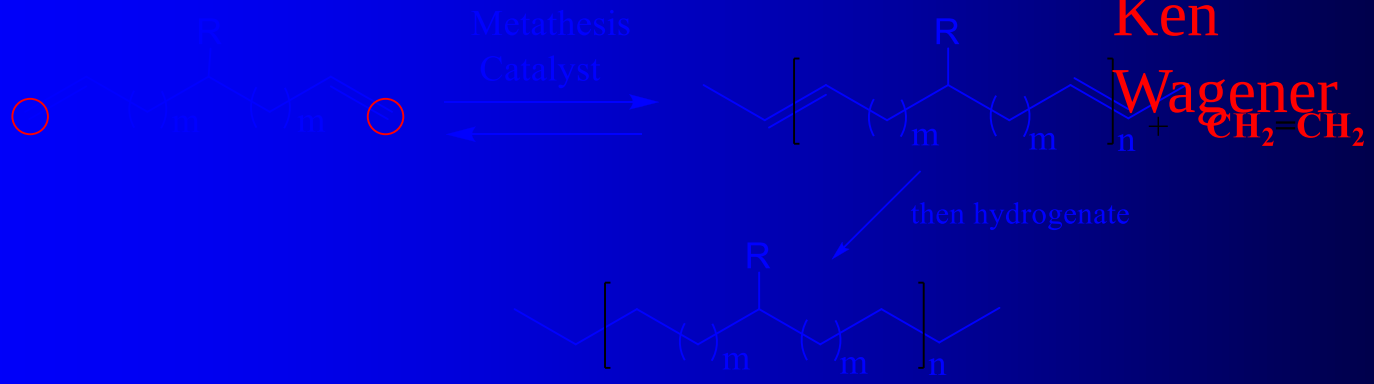
Richard Schrock
Massachusetts Institute
of Technology (MIT)
Cambridge, MA, USA

http://nobelprize.org/chemistry/laureates/2005/index.html

ADMET is step growth polymerization chemistry

Ken Wagener

Symmetrical Diene

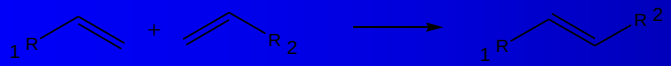


Symmetrical Repeat Unit

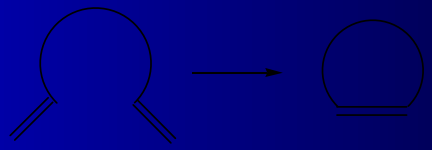
- **High strength polymers can be made by ADMET**

Span of Olefin Metathesis

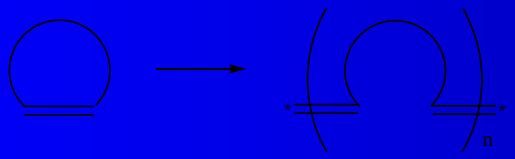
Types of Metathesis



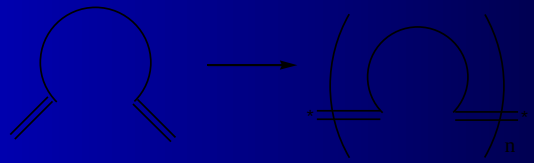
cross metathesis (CM)



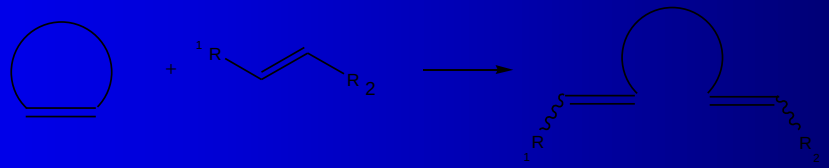
ring closing metathesis (RCM)



ring opening metathesis polymerization (ROMP)



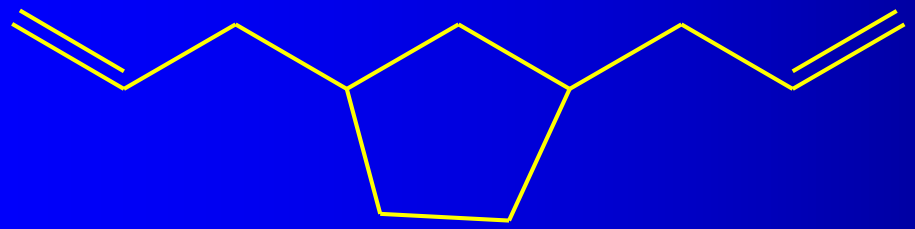
acyclic diene metathesis (ADMET)



ring opening cross metathesis (ROCM)

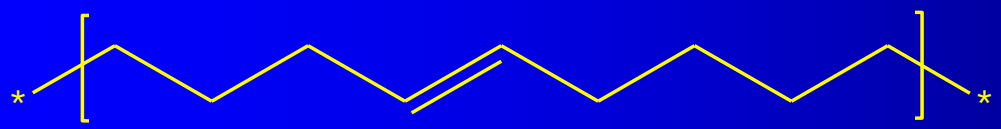
C.W. Bielawski, R.H. Grubbs *Prog. Polym. Sci.* 32 (2007) 1.

Lets Practice ADMET



Catalyst

Vacuum



$H_2C{=}CH_2$

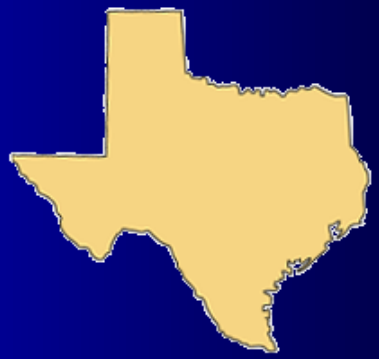
Catalyst, BIG pressure

Plastic

Americans use 2,500,000 plastic bottles every hour. Most of them are thrown away.

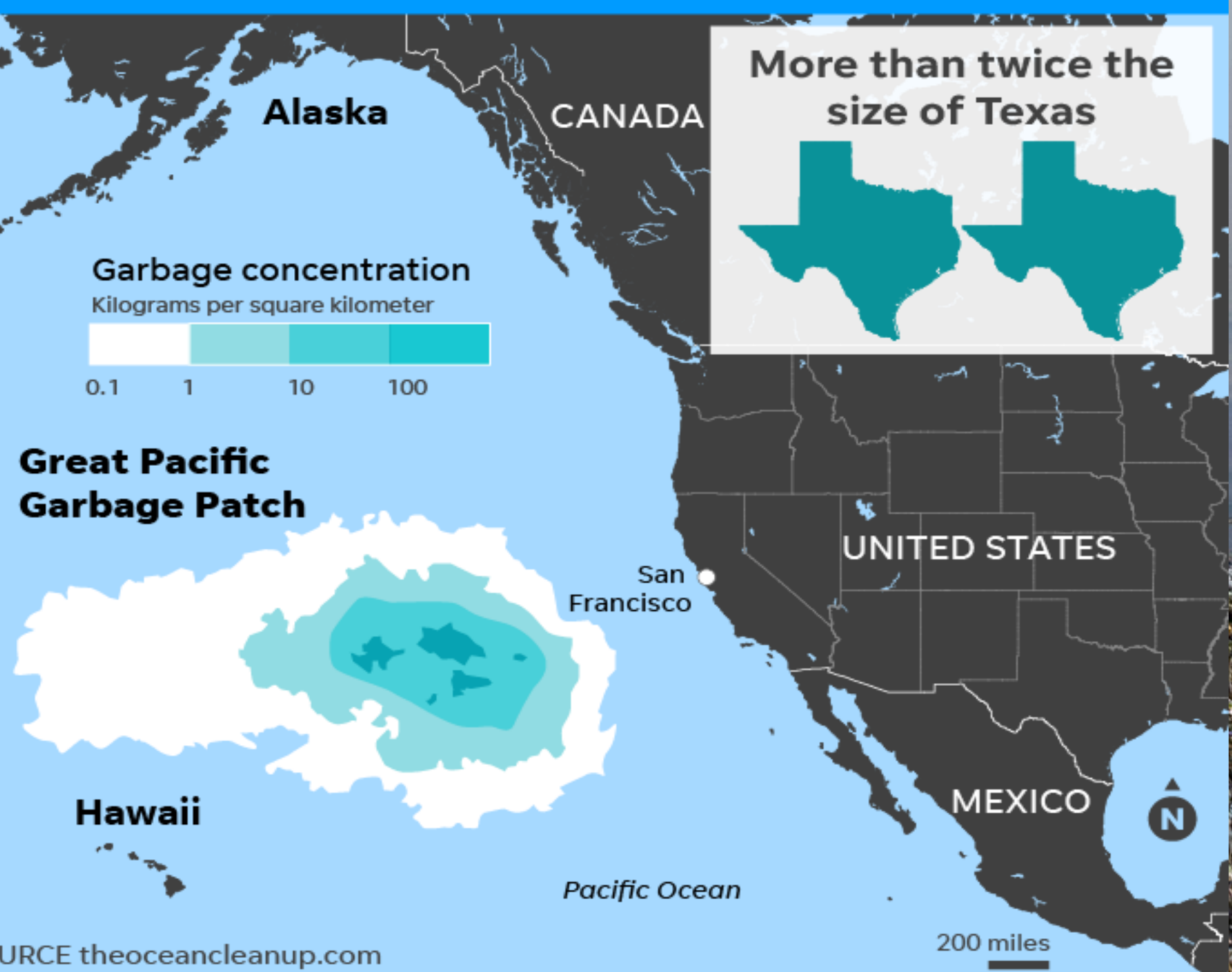
Five 2-liter recycled PET bottles provide enough fiberfill for a ski jacket.

Every year, we make enough plastic film to shrink-wrap the state of Texas.



Recycling plastic saves twice as much energy as burning it in an incinerator.

What becomes of this stuff??


Alaska
CANADA
More than twice the size of Texas
Garbage concentration
Kilograms per square kilometer
0.1
1
10
100
Great Pacific Garbage Patch
UNITED STATES
San Francisco
MEXICO
N
Hawaii
Pacific Ocean
200 miles
URCE theoceancleanup.com

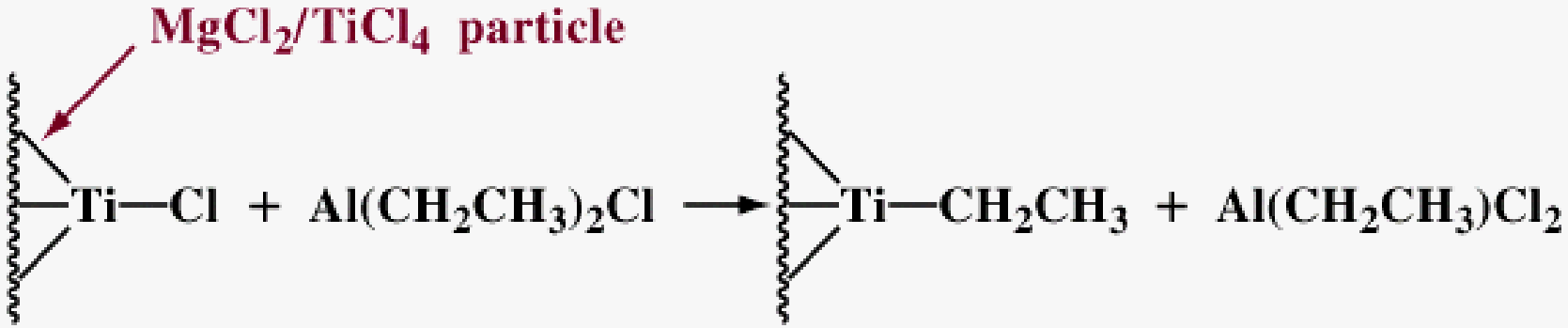
Caribbean Crisis

Plastic Identification Code	Type of plastic polymer	Properties	Common Packaging Applications
	Polyethylene Terephthalate (PET, PETE)	Clarity, strength, toughness, barrier to gas and moisture.	Soft drink, water and salad dressing bottles; peanut butter and jam jars
	High Density Polyethylene (HDPE)	Stiffness, strength, toughness, resistance to moisture, permeability to gas.	Water pipes, Hula-Hoop (children's game) rings, Milk, juice and water bottles; the occasional shampoo / toiletry bottle
	Polyvinyl Chloride (PVC)		
	Low Density Polyethylene (		.g. honey, mustard; cling
	Polypropylene (PP)	barrier to moisture.	ware; yogurt containers; ble take-away containers; disposable cups and plates.
	Polystyrene (PS)	Versatility, clarity, easily formed	Egg cartons; packing peanuts; disposable cups, plates, trays and cutlery; disposable take-away containers;
	Other (often polycarbonate or ABS)	Dependent on polymers or combination of polymers	Beverage bottles; baby milk bottles; electronic casing.

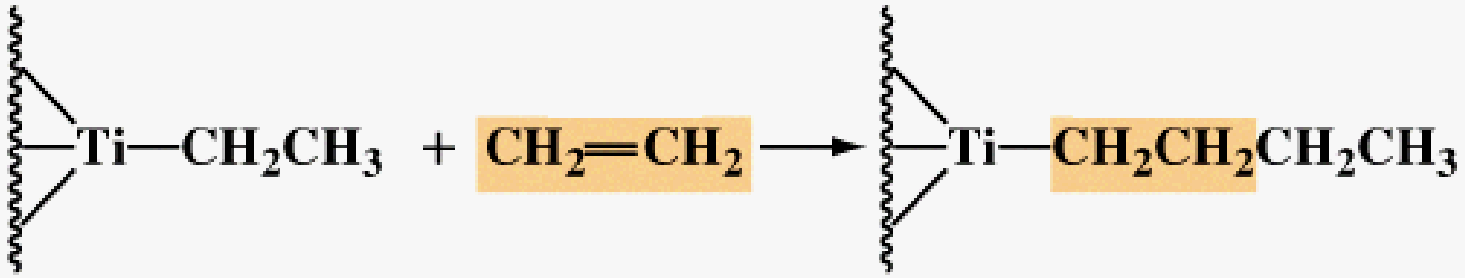
PLEASE RECYCLE

Mechanism: Ziegler-Natta catalysis of alkene polymerization

Step 1: **Formation of a titanium-ethyl bond**

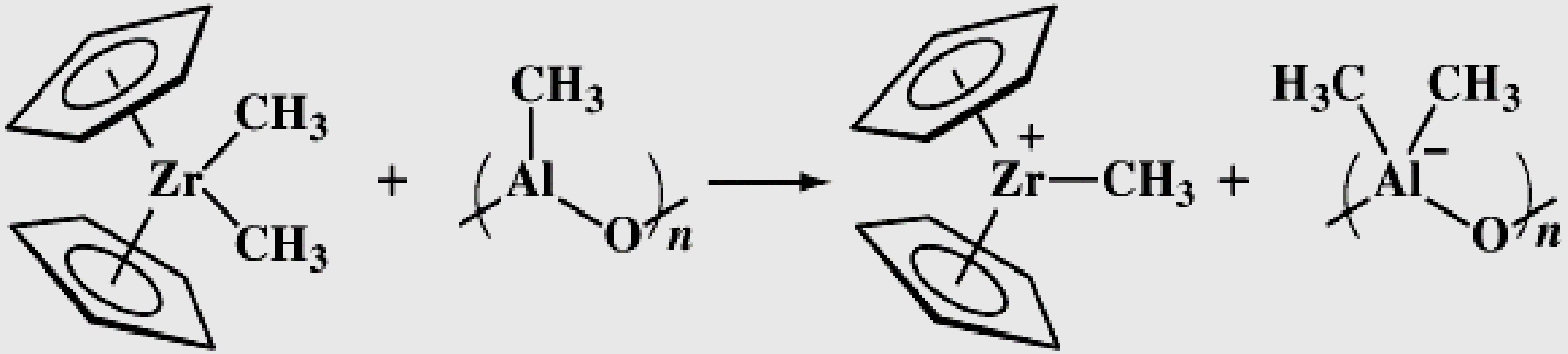


Step 2: **Insertion of ethylene into the titanium-carbon bond**



Mechanism: Ziegler-Natta coordination polymerization of an alkene

Step 1: Activation of the zirconium catalyst

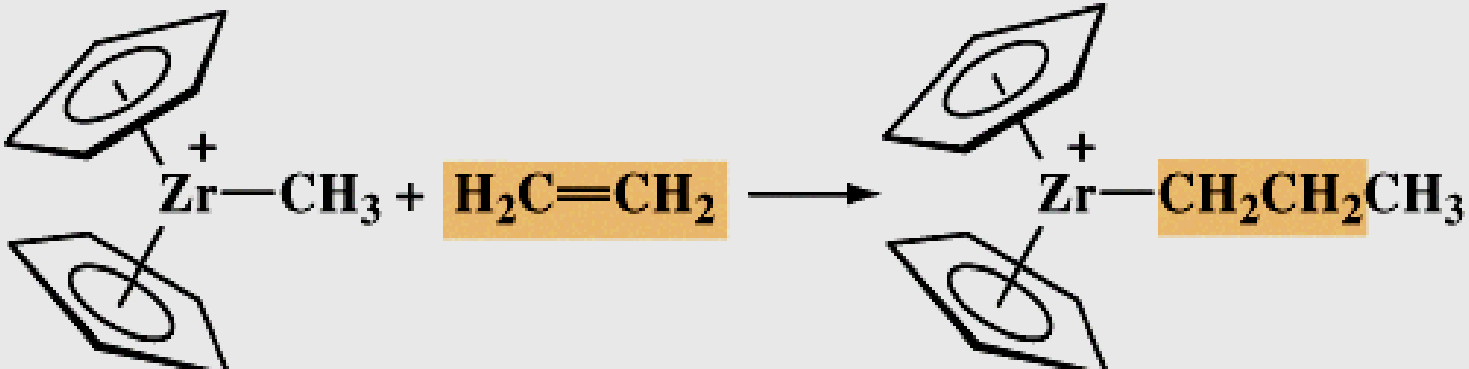


Bis(cyclopentadienyl)-dimethylzirconium

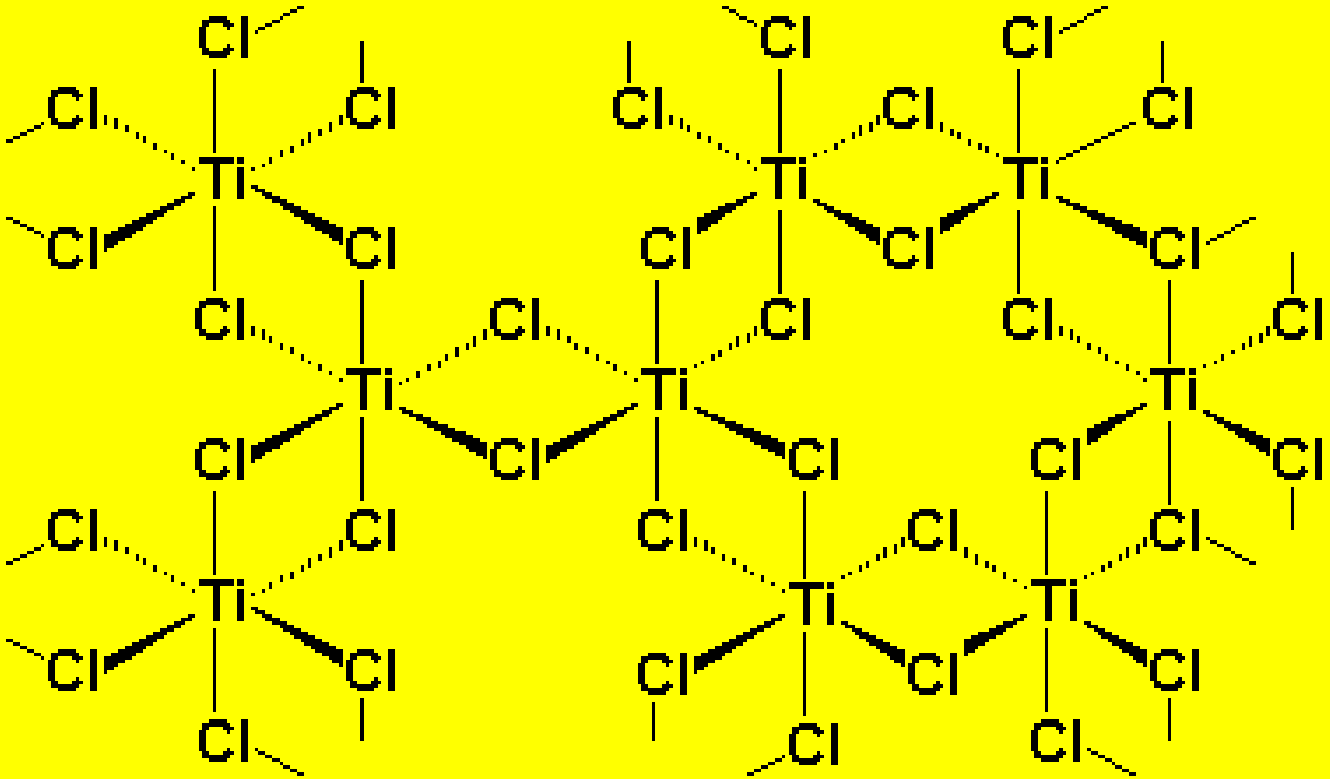
MAO

A zirconium cation (the active form of the catalyst)

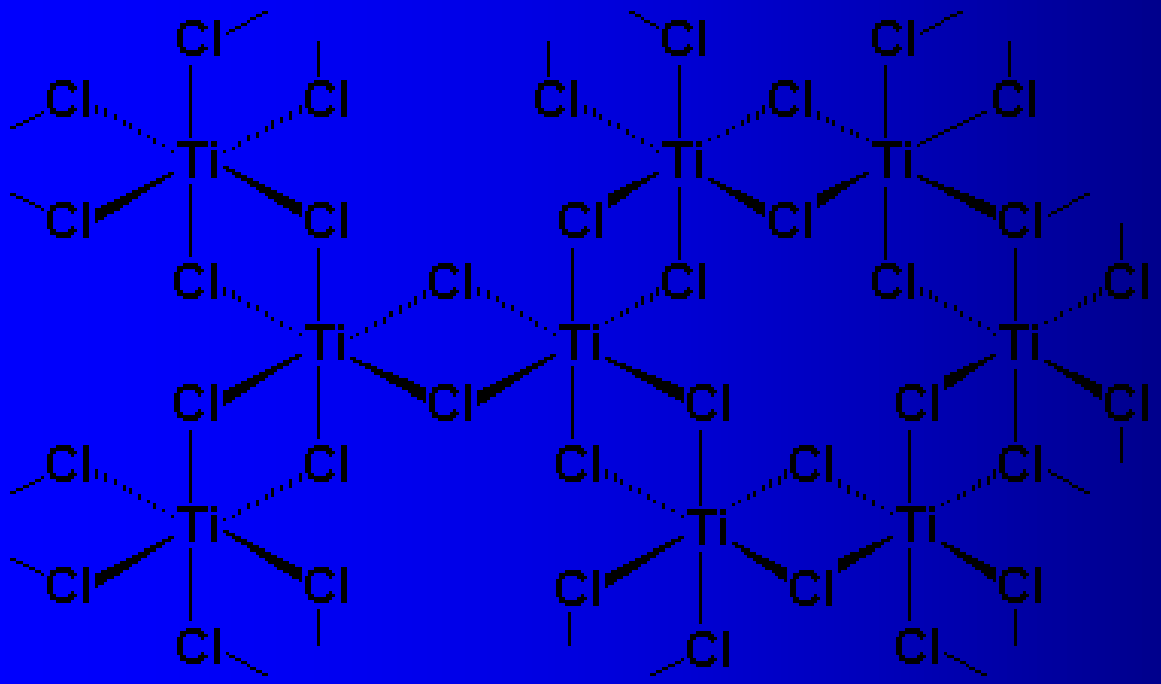
Step 2: Insertion of ethylene monomers into the zirconium-carbon bond



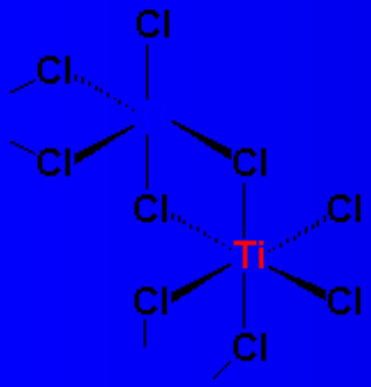
The Catalyst



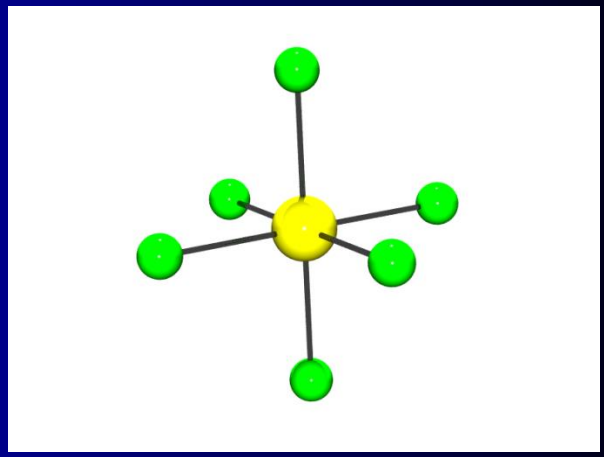
a crystal of α-$TiCl_3$



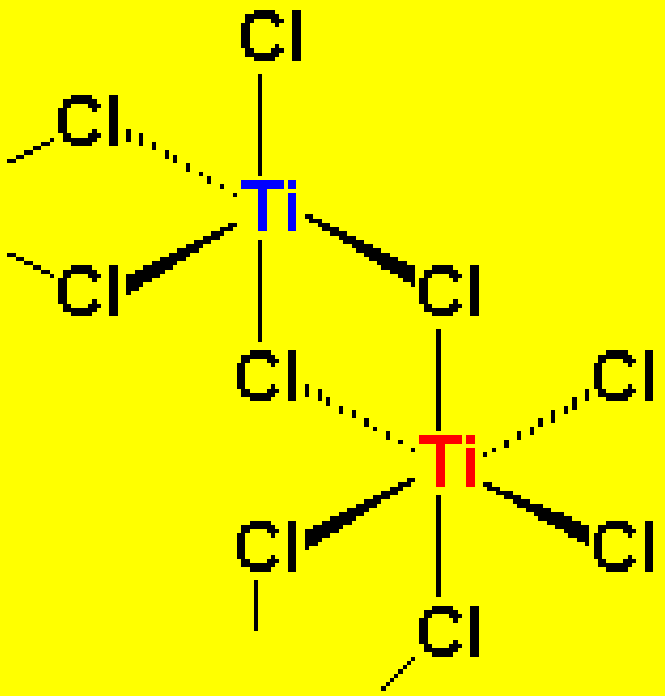
a crystal of α-$TiCl_3$



While the titanium on the interior (in red) has six chlorine neighbors, the surface titanium (blue) only has five.



The Catalyst



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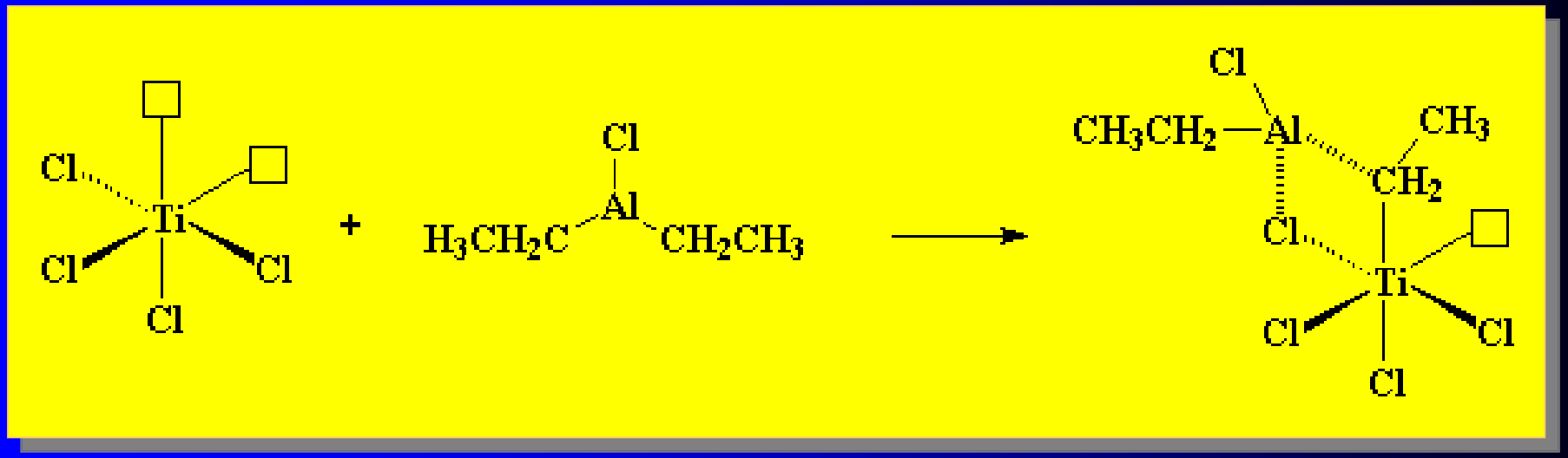
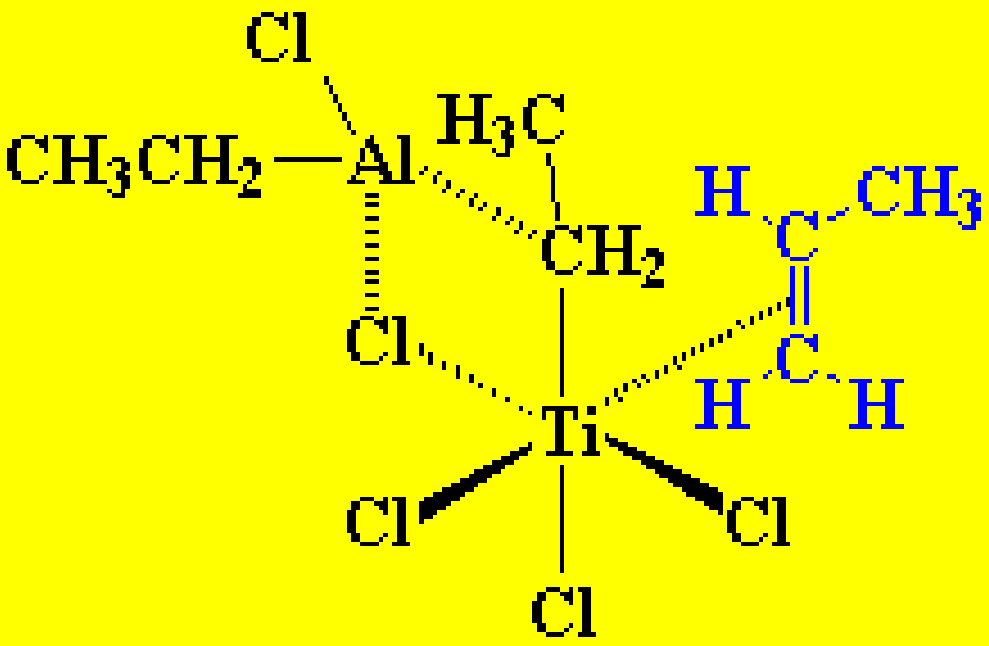
The Catalyst

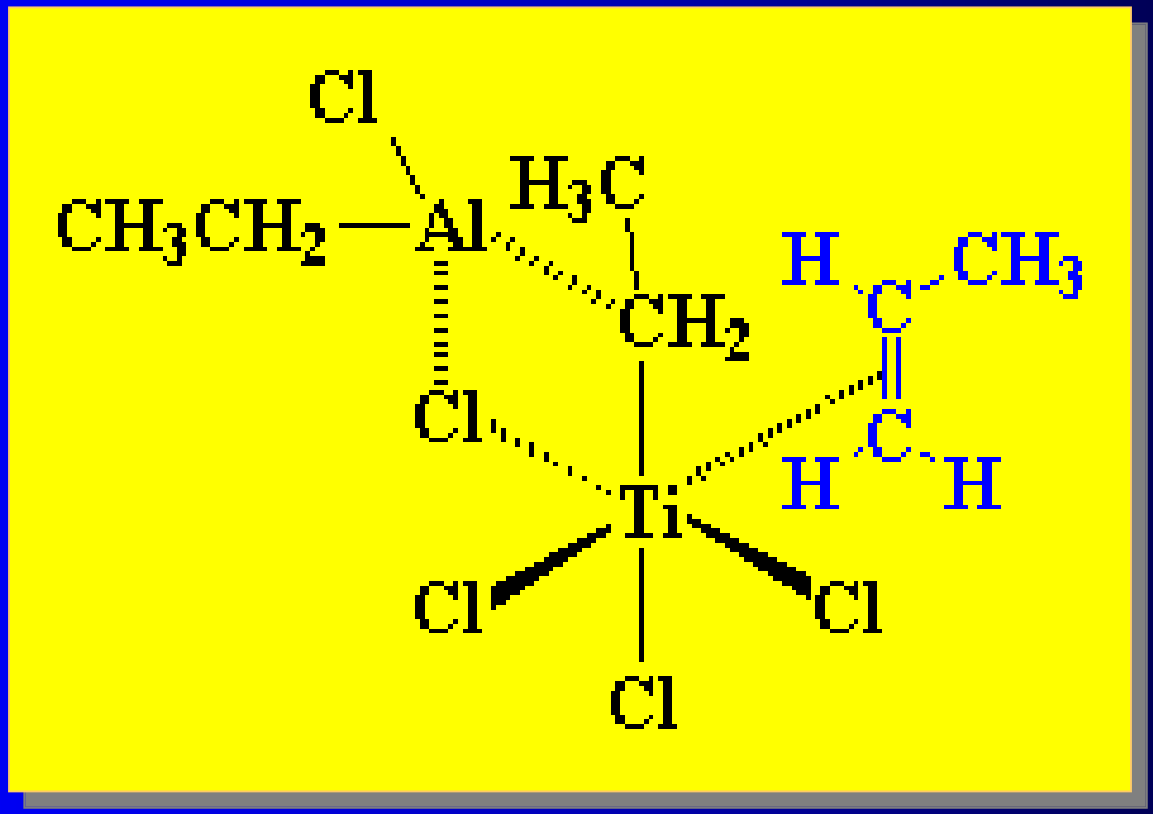


The Catalyst



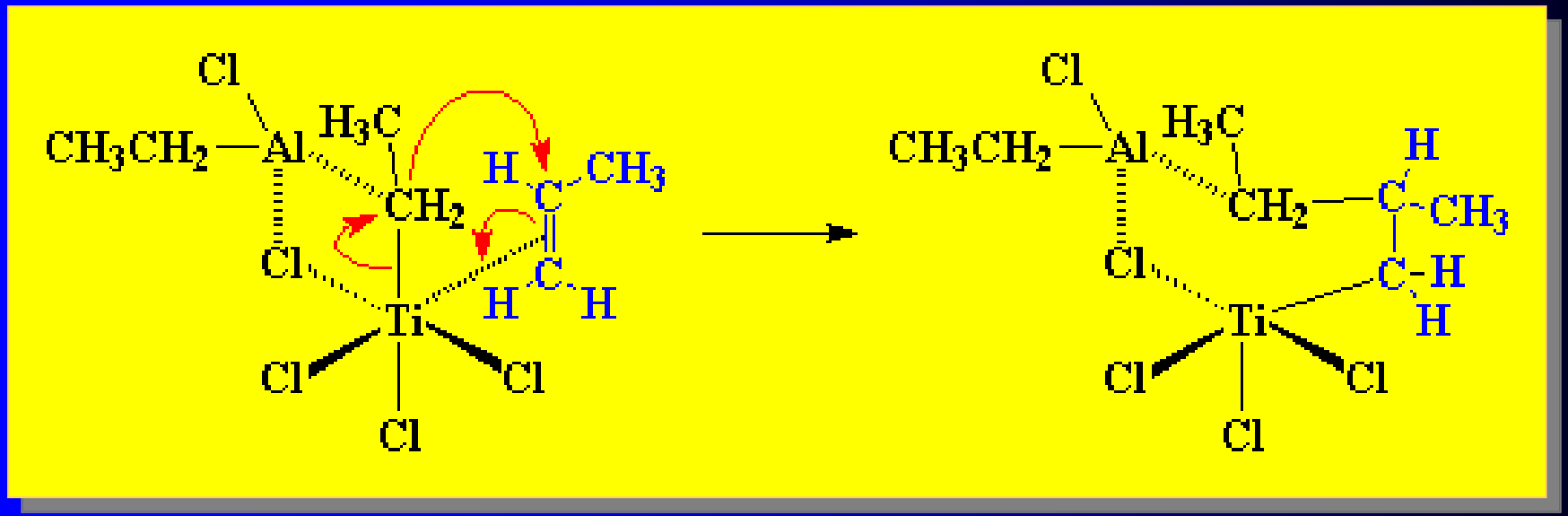
The π-electrons from propylene end up filling titanium's empty orbital.

The Catalyst



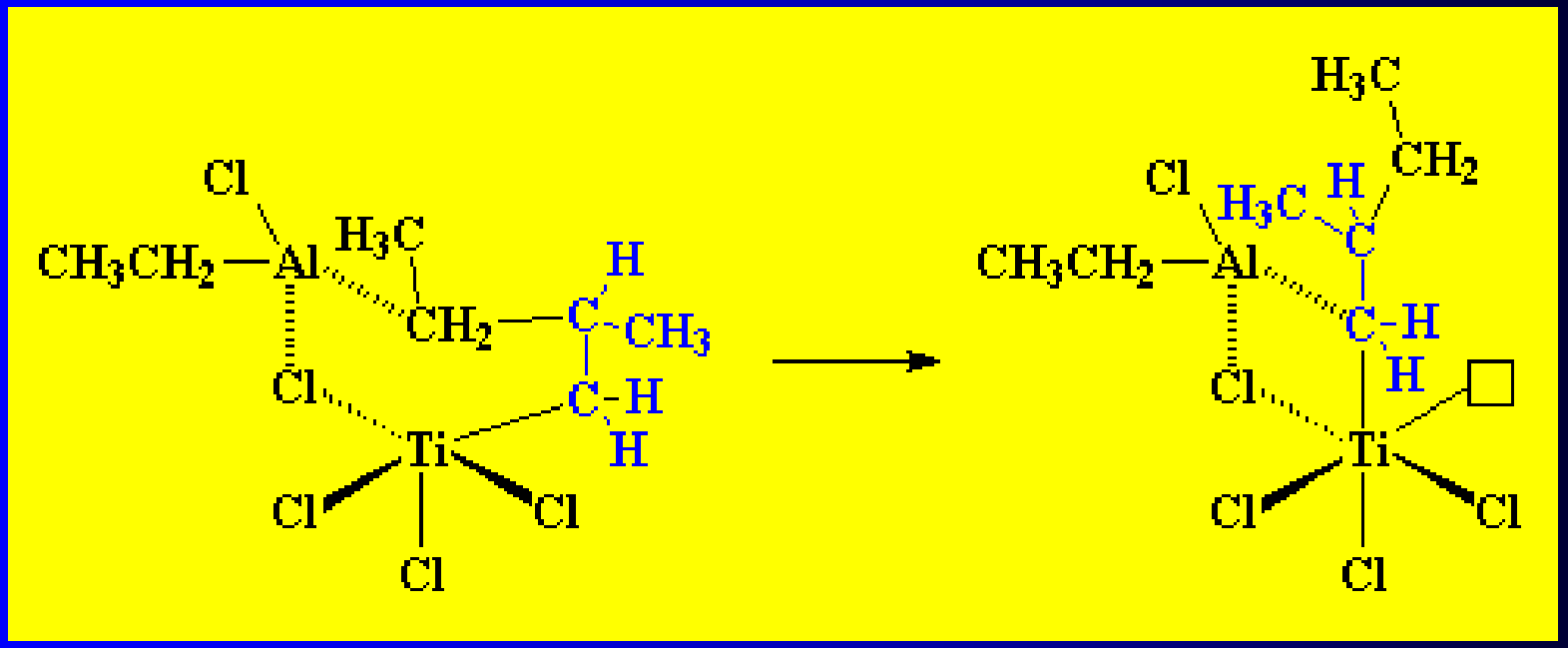
….note the steric demand …

Alkene Addition to the Catalyst



There occurs a “shift” as shown

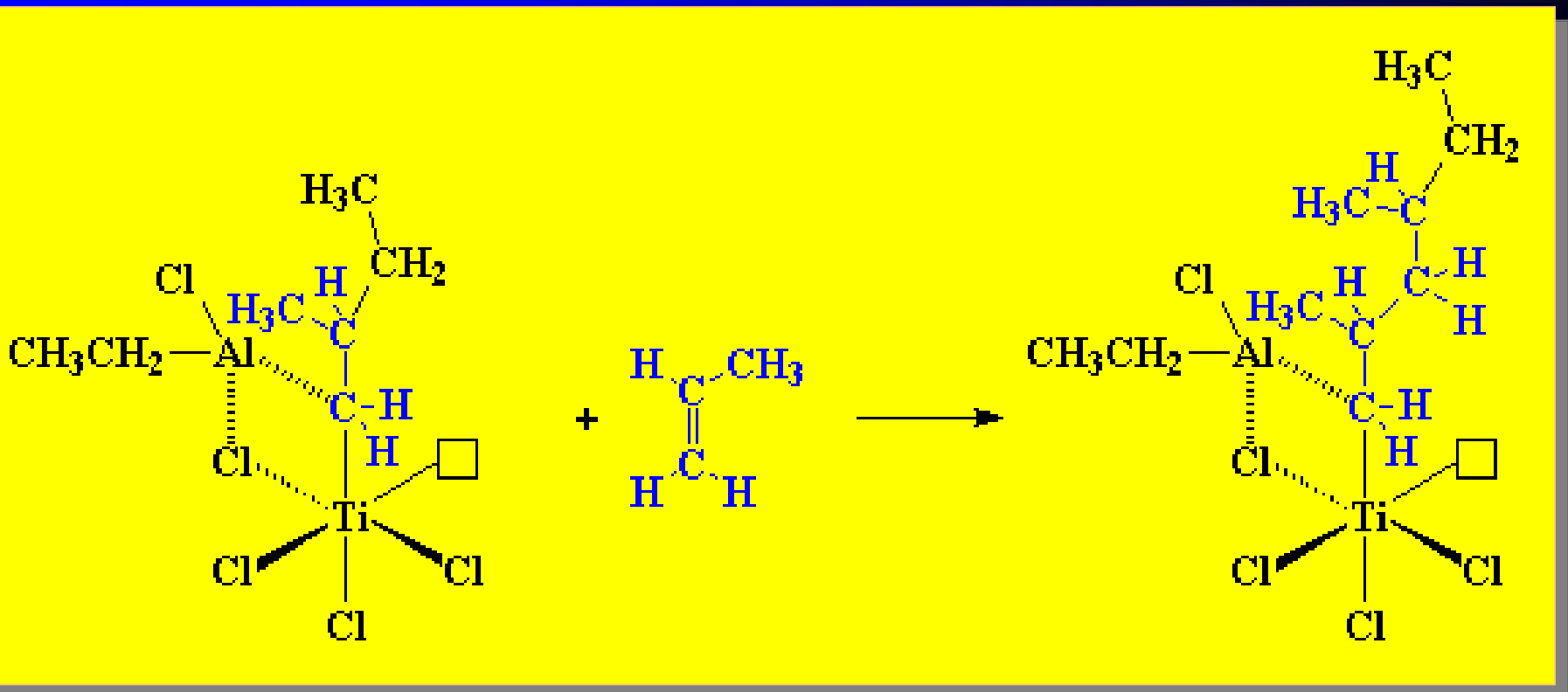
The “shift”



Now Ti has an empty orbital again and there is an Al-C complex formed to the monomer

Propagation

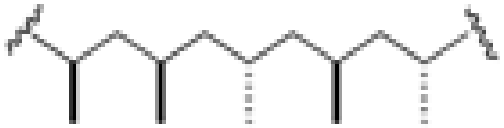
Another alkene is added and the process repeats



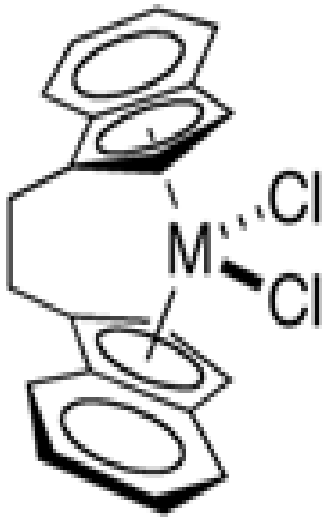
Steric demand leads to isotactic polymer

The Kaminsky Catalysts 1980

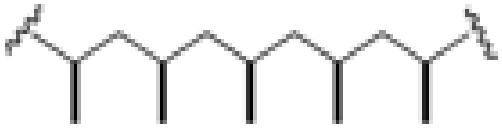
1, M = Zr, Hf



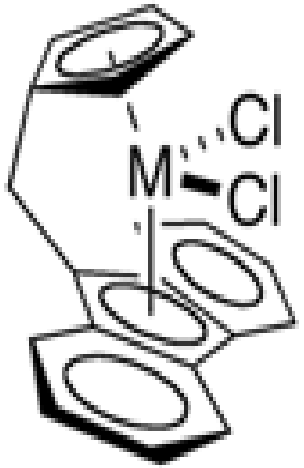
atactic polypropylene



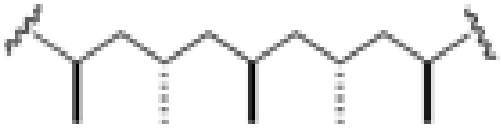
2, M = Zr, Hf



isotactic polypropylene



3, M = Zr, Hf



syndiotactic polypropylene