Polymer Fundamentals

Overview

Types of Polymers
Polymer Synthesis
Molecular Architecture

Rosen Chapters

II, III, IV, IX, X, XI, XII

Types of Polymers

Greek "polys" → many "meros" → parts

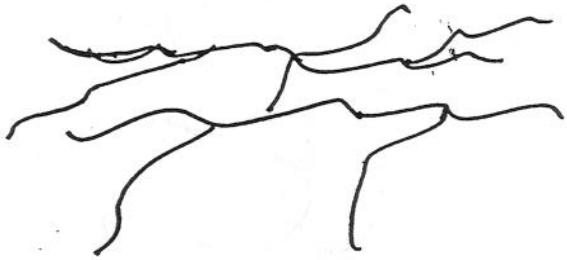
Structure. Polyethylene (PE)

Linear

HDPE

Branched

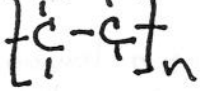
short-chain branching
(linear Low Density P
LLDPE



Long-chain brand
(Low density PE
LDPE

Homopolymer Polymer composed of only one repeating unit.

$-[AAAAAA]_n$



PE

Polystyrene (PS)

Copolymer repeating unit from two or more monom

random AABABBAAABBAB (ideal)

Alternating ABABABABAB

block AAAAABBBBB AAAAA BBBBB

diblock AAAAAAABBBBBBBB

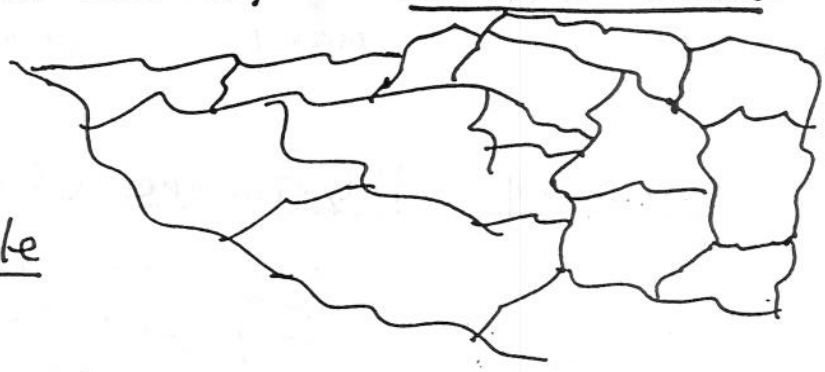
triblock AAAAAABBBBBBCC

graft AAAAAAAAAA
BBBBBB BBBBBB

Polymer Definitions.

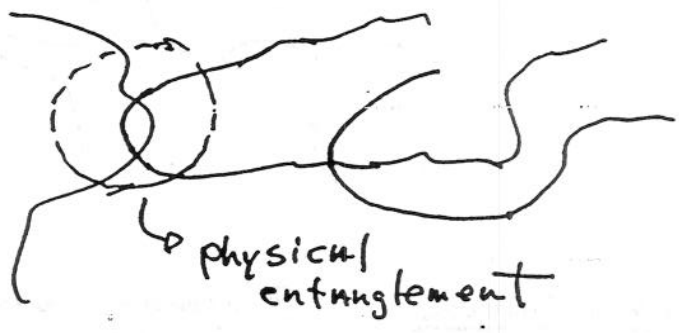
Crosslinked (Network) **Covalent Bond.**

one giant molecule



Example: Rubber (Elastomer)

* entanglement * Physical Crosslink.



thermoplastic :
- soften and flow upon heating
- can be re-melted and reformed repeatedly.
- most commercial polymers are thermoplastics (PE, PS, PET, etc.)

thermosets :
- materials which do NOT flow upon heating
- usually crosslinked materials
- Examples: vulcanized rubber tires
  rubber bands

Polymer Definitions.

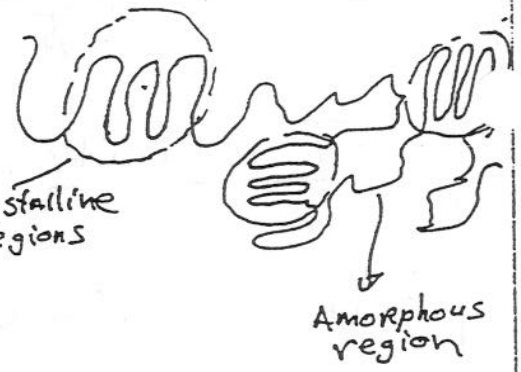
Amorphous (glassy) Polymer. [Clear]

- non-crystalline polymers or non-crystalline regions in a polymer.

e.g., PS, PVC
Polycarbonate (PC)
Polymethylmethacrylate
PMMA → Plexiglass®

Crystalline Polymer. [translucent]

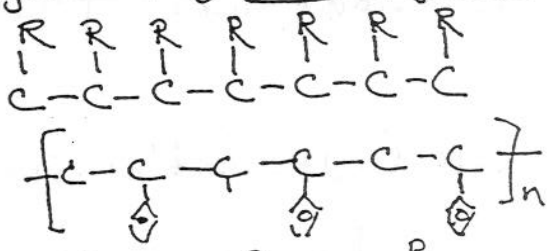
- highly ordered regions in polymer.
- NO polymers are 100% crystalline — there are always some amorphous tie regions



* $\boxed{\text{Semi-Crystalline}}$ Polymer

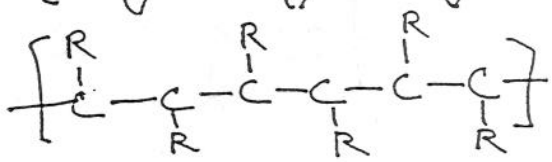
Tacticity Arrangement of pendant groups in space.

isotactic

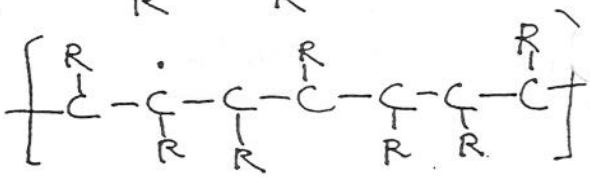


isotactic PS

syndiotactic



Atactic (random)



Stereoisomerism

Polyethylene $\left[-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\right]_n$ symmetrical, tetra

planar "zig-zag" conformation

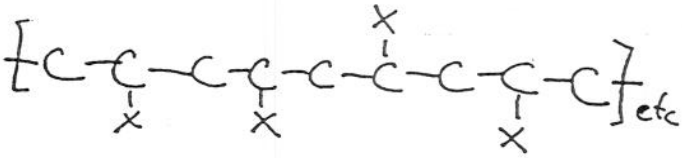
Vinyl Monomers $H-\underset{H}{C}=\underset{X}{C}-H$

- polymerize in head-to-tail fashion ∴ X group always on every other C group.

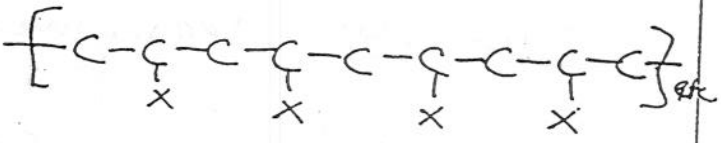
$$\left[-\underset{H}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}-\right]_n$$

Tacticity: arrangement of pendant groups in space.

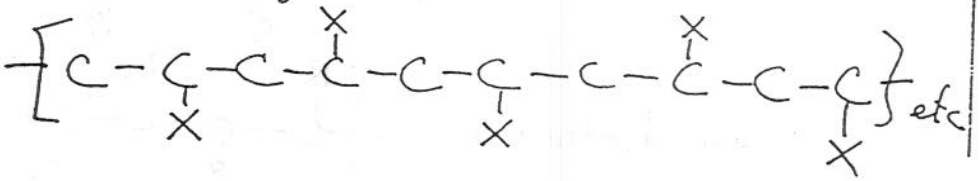
Atactic (random)



Isotactic (same side)



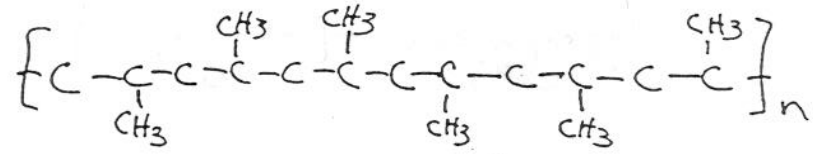
Syndiotactic (alternating sides)



Dr. Giulio Natta – 1964 Nobel Prize in Chemistry for work in this area.

Stereoregularity (or lack of it) effects Mechanical Properties

Example: Polypropylene (PP) $\left[C-\underset{CH_3}{\underset{|}{C}}\right]_n$

Atactic 

- consistency of chewing gum. (amorphous

isotactic or syndiotactic → hard, rigid plastics (semi-crystalline

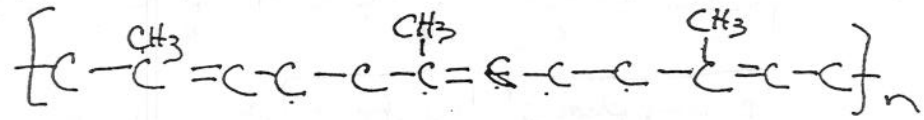
Which forms used for PP bottles?

Stereoisomerism in Diene Polymers

- due to inability to rotate around double bond.

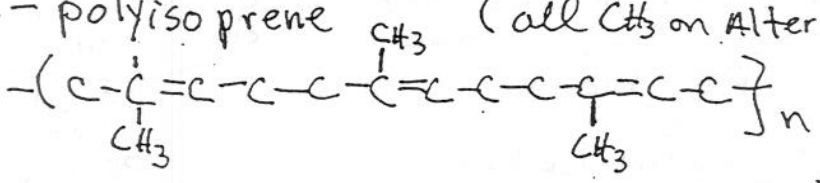
Polyisoprene $\left[C-\overset{CH_3}{\overset{|}{C}}=C-C\right]_n$ 1,4 PI

cis-polyisoprene (all CH_3 groups on same side)



- natural rubber (rubber bands)

trans-polyisoprene (all CH_3 on alternating sides)



- gutta-percha rubber (tough, not elastic) — golf ball covers

Example 5.3 (Rosen) Effect of Crystallinity on Mechanical Properties and Optical Properties

Facts.

① polyethylene (PE) $\left[\overset{|}{C}-\overset{|}{C}\right]_n$

polypropylene (PP) $-\left[-\overset{|}{C}-\overset{|}{\underset{CH_3}{C}}\right]_n$

} when produced with "stereospecific catalysts" rigid, translucent

- 65-35 copolymer of PE/PP is a soft, transparent rubber

② A plastic which is rigid and translucent (similar to PE or PP) is composed of 65% E and 35% P units.

Question: How can this be true?

① PE is linear ⇒ highly crystalline

PP is isotactic $\left[C-\underset{CH_3}{C}-C-\underset{CH_3}{C}-C-\underset{CH_3}{C}-C-\underset{CH_3}{C}\right]_n$ ⇒ highly crystal

- 65-35 copolymer (ethylene-propylene rubber EPR) is a Random Copolymer.

$$\left[\overset{PE}{C}-C-\overset{PP}{C}-\underset{CH_3}{C}-\overset{PP}{C}-\underset{CH_3}{C}-\overset{PE}{C}-C-\overset{PP}{C}-\underset{CH_3}{C}-\overset{PE}{C}-C-\overset{PP}{C}-\underset{CH_3}{C}-\overset{PP}{C}-\underset{CH_3}{C}-\overset{PE}{C}-C\right]$$

$\boxed{\text{Amorphous}}$, $\boxed{\text{rubbery}}$ material

② 65-35 EPR ⇒ Block copolymer:

$$\left[\underbrace{\overset{PE}{C}-C-\overset{PE}{C}-C-\overset{PE}{C}-C-\overset{PE}{C}-C-\overset{PE}{C}-C}_{\text{PE block}}-\underbrace{\overset{PP}{C}-\underset{CH_3}{C}-\overset{PP}{C}-\underset{CH_3}{C}-\overset{PP}{C}-\underset{CH_3}{C}-\overset{PP}{C}-\underset{CH_3}{C}-\overset{PP}{C}-\underset{CH_3}{C}}_{\text{PP block}}\right]_n$$

PE block ⇓ PE crystal lattice

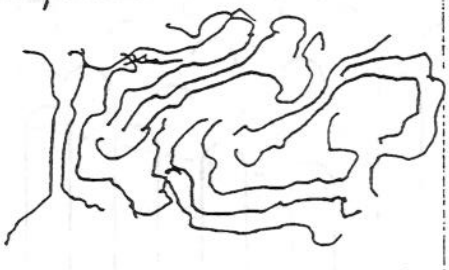
PP block ⇓ PP crystal lattice

- rigid, translucent

Polymer Morphology (Rosen, Ch. V)

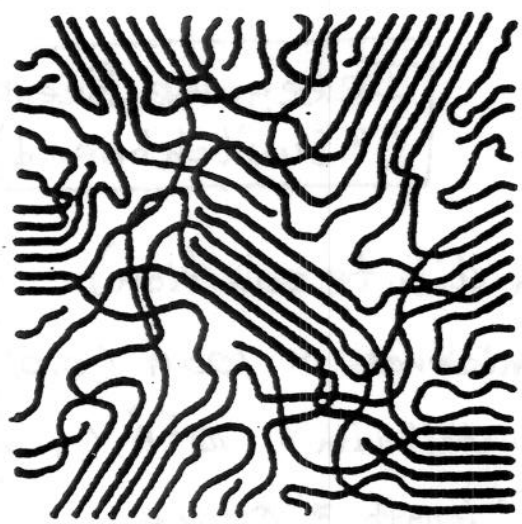
Amorphous vs Crystalline (semi-)

entangled, random coil

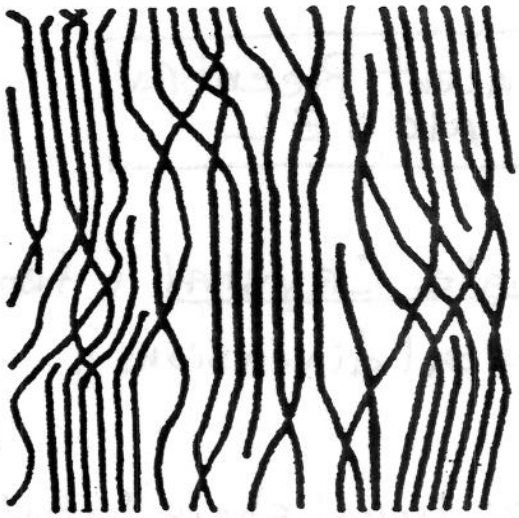


entangled, Aligned regions

Fringed Micelle Model



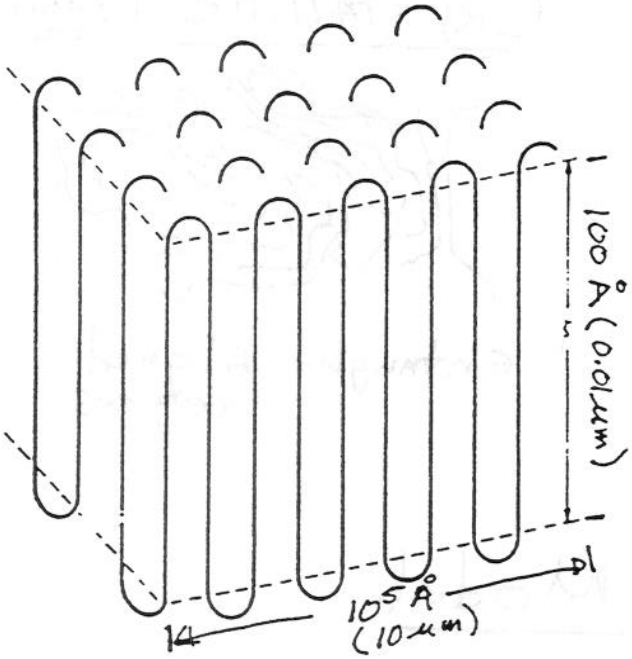
UNORIENTED

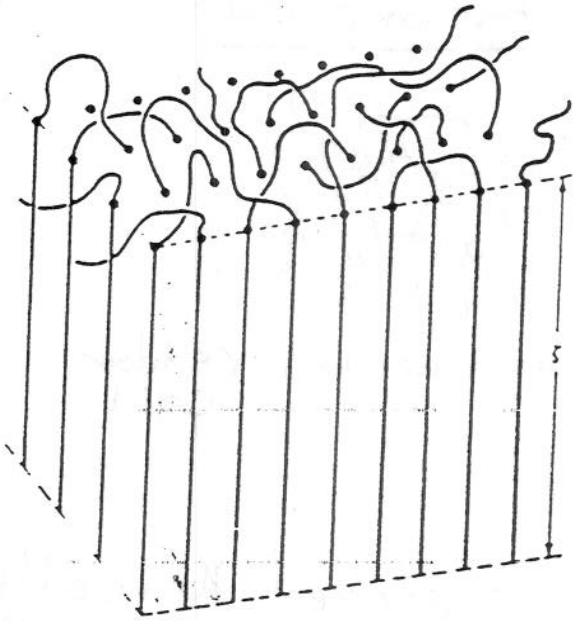


ORIENTED (stress field)

- "ORDERED DOMAINS" connected by "Amorphous" regions
- origin of the SEMI-CRYSTALLINE nature
- typical (high) crystallinity ≈ 85%
- effect of crystallinity on MECHANICAL Properties similar to cross-linking (but can be melted)

Lamellar Crystals (Chain Folded Model)





Adjacent Reentry MODEL

Irregular Reentry ("Switchboard)

Single Crystal (from dilute solution)

- typical dimensions: thickness ≈ 100 Å (0.01 μm)
  Length/Width ≈ 10^5 Å (10 μm)

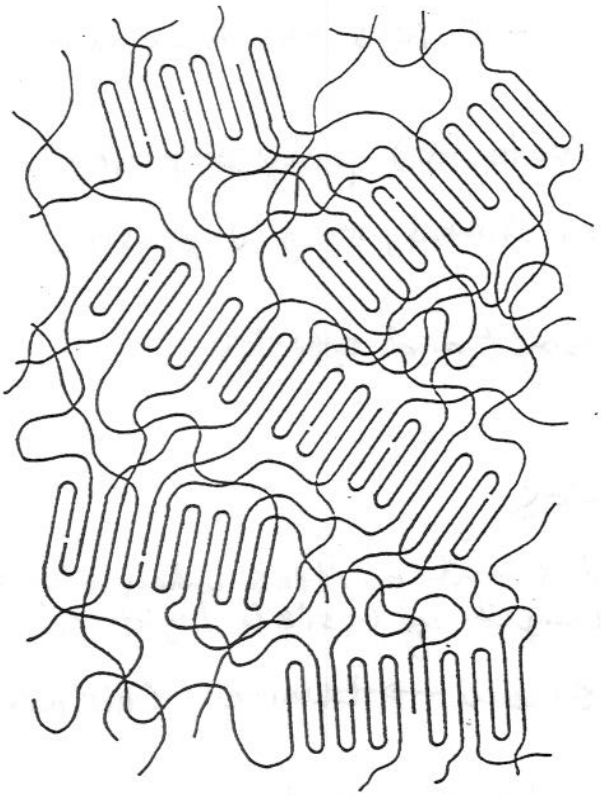
*Note: typical chain "extended" length ≈ 0.1 μm.

Bulk (Melt) Crystallized.

- typical dimension: up to 1 μm (10^4 Å) thick.
- Most often "Switchboard" Reentry

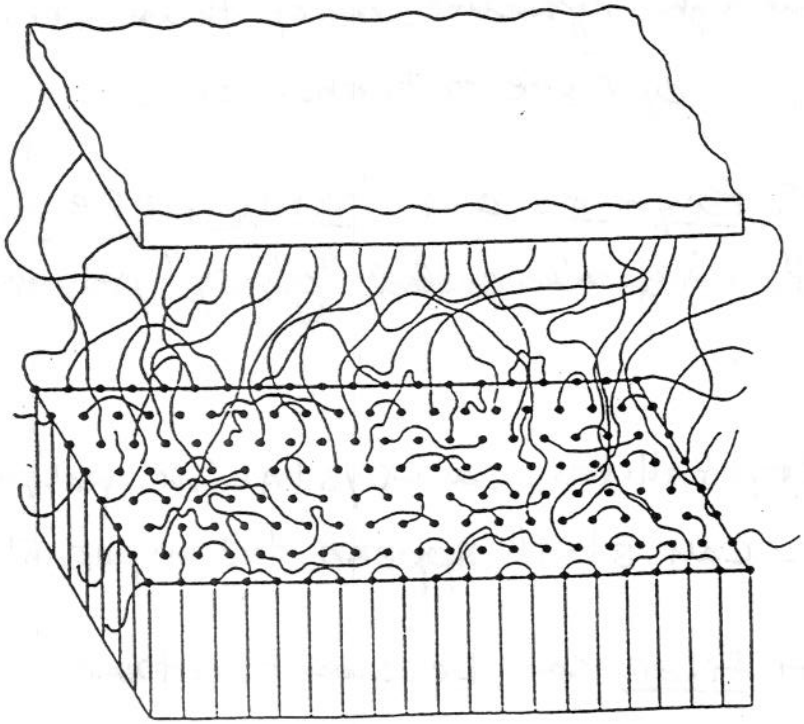
Chain-folded Lamella with Amorphous Tie Molecules

Model for Melt Crystalized Polymers



2-D Perspective.

- chain-folded (aligned) regions
- amorphous interlamellar Region
- very little Adjacent reentry



3-D Perspective (side view)

- "Switchboard" REENTRY

Crystallinity Effects.

① Mechanical Properties (Refer to Table 5.1)

- increased <u>strength</u> and <u>rigidity</u>.
- greater ratio crystalline / Amorphous
  - → stronger → more rigid
  - → harder → less easily deformed.

E.g. Stereoregular (isotactic) polypropylene.
- crystallizable: hard, rigid plastic

Atactic PP
- Amorphous, soft and sticky.

② Optical Properties.

- light scattering at discontinuities when the size similar to wavelength of visible light (0.4–0.7μ...)

  ice → clear snow → white (air/crystal interfa

- semi-crystalline polymer → dense crystalline regions have higher refractive index than amorphous regions ∴ opaque or translucent

- <u>AMORPHOUS</u> <u>Polymers</u> are <u>transparent</u>.
  ↳ that's why also called "glassy" polymers

<u>Exceptions.</u>

- very small crystallites in a crystalline polymer → the polymer can still appear transparent.

- <u>copolymer</u> or <u>filler</u> can be cause for translucent

Effect of Crystallinity on Mechanical Properties.

ıble 5.1 The Influence of Crystallinity on Some of the Properties of Polyethylene[a]

rcial product	Low density	Medium density	High density
ensity range, g/cm^3	0.910–0.925	0.926–0.940	0.941–0.965
pproximate % crystallinity	42–53	54–63	64–80
ranching, equivalent CH_3 groups/1000 carbon atoms	15–30	5–15	1–5
rystalline melting point,°C	110–120	120–130	130–136
ardness, Shore D	41–46	50–60	60–70
ensile modulus, psi	$0.14–0.38 \times 10^5$	$0.25–0.55 \times 10^5$	$0.6–1.8 \times 10^5$
(N/m^2)	$(0.97–2.6 \times 10^8)$	$(1.7–3.8 \times 10^8)$	$(4.1–12.4 \times 10^8)$
ensile strength, psi	600–2300	1200–3500	3100–5500
(N/m^2)	$(0.41–1.6 \times 10^7)$	$(0.83–2.4 \times 10^7)$	$(2.1–3.8 \times 10^7)$
lexural modulus, psi	$0.08–0.6 \times 10^5$	$0.6–1.15 \times 10^5$	$1.0–2.6 \times 10^5$
(N/m^2)	$(0.34–4.1 \times 10^8)$	$(4.1–7.9 \times 10^8)$	$(6.9–18 \times 10^8)$

It must be kept in mind that mechanical properties are influenced by factors other than the degree of crystallinity (molecular wei particular).

Density: crystalline regions more DENSE than Amorphous

$$\frac{1}{\rho} = \frac{w_c}{\rho_c} + \frac{w_a}{\rho_a}$$

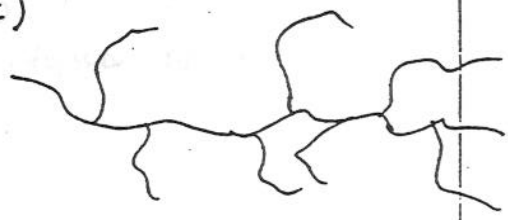
(c = crystalline
a = amorphous)

- density is a quick relative measure of crystallinity.

Polyethylene.

→ Low Density Polyethylene (LDPE)

- Long-chain branching



→ Linear Low Density PE (LLDPE): misnomer

- short chain branching
- Medium density
- copolymer (vinyl monomers)

→ High Density PE (HDPE)

- linear

Examples

① Polystyrene (atactic) → transparent
- random phenyl group arrangement

② Polystyrene (isotactic) → white
crystallizes

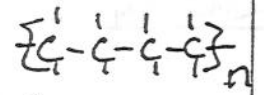
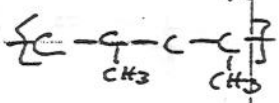
③ High Impact PS (dispersion of ~~the~~ polybutadiene rubber particles) → white

Problem.

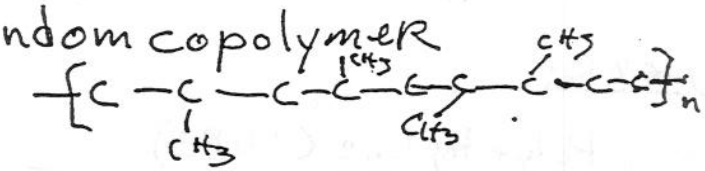
→ PE and PP produced by stereospecific catalysts
- fairly rigid, translucent plastics.

→ 65/35 copolymer blend → soft, transparent rubber.

Why?

- PE linear → highly crystalline 
- PP isotactic → highly crystalline 
- 65/35 copolymer: Ethylene-Propylene Rubber (EPR)

→ random copolymer



- amorphous, rubbery polymer.

ELASTOMERIC POLYPROPYLENE

Oscillating catalyst controls microstructure

Unprecedented control over the microstructure of polypropylene has been achieved by Stanford iversity chemists through use of an illating catalyst that, depending on its information, promotes two different es of propylene polymerization.

The catalyst produces polypropyl- with a wide range of elastic prop- ies, according to the polymerization nditions.

The catalyst is the first example of a w, inexpensive approach to producing ck copolymers, says associate profes- of chemistry Robert M. Waymouth, o carried out the research with grad- e student Geoffrey W. Coates. Unlike dinonal routes to block copolymers— hich a catalyst polymerizes different sequentially—the new cata- izes a single monomer in 5 qu. nt ways [*Science*, 267, 222 95)].

Moreover, the product—elastomeric ypropylene—has real commercial ential, Waymouth notes. "Because stomeric polypropylene is a ther- oplastic, it is recyclable," he explains. is an elastomer only until it melts a temperature higher than its use nperature."

By contrast, conventional thermoset bers, whether natural or synthetic, ive their elasticity from covalent s-linking of polymer chains. Because hese covalent bonds, rubbers cannot recycled by melt processing.

Kenneth B. Wagener, a chemistry pro- sor at the University of Florida, nesville, points out in a commentary he same issue of *Science* (page 191) t polypropylene is the product of k in the 1950s by Karl Ziegler and lio Natta, who discovered a method producing stereoregular polypropyl- using a chiral catalyst. Ziegler and ta shared the 1963 Nobel Prize in emistry for their work on polymers.

Today, polypropylene is one of the largest volume plastics in use. vertheless, Wagener observes, the work by Waymouth and Coates demonstrates that "even such a mature material as polypropylene can be the subject of dramatic advances in polymer chemistry."

Waymouth and Coates note that the stereochemistry of polyolefins, which can be described in terms of their "tacticity," strongly influences their properties. Isotactic polypropylene, in which all of the stereocenters of the polymer are the same, is a crystalline thermoplastic. By contrast, atactic polypropylene, in which the stereocenters are arranged randomly, is an amorphous gum elastomer.

Polypropylene consisting of blocks of atactic and isotactic stereosequences is rubbery. Although previous researchers have discovered catalysts that produce elastomeric polypropylene, "it has so far proven difficult to control the polymer structure and properties through a rational modification of the catalysts or reaction conditions," Waymouth says.

Waymouth and Coates built on the work of other researchers who showed that rigid, chiral metallocene catalysts produce isotactic polyolefins, whereas achiral forms of the catalysts produce atactic polyolefins. Their research was supported by Amoco and the National Science Foundation.

The Stanford chemists prepared an unbridged metallocene catalyst with indenyl ligands that rotate about the metal-ligand bond axis. The rotation causes the catalyst to isomerize between chirallike and achirallike geometries.

When the catalyst is in the chirallike geometry, it synthesizes a block of isotactic polypropylene; when it is in the achirallike geometry, it generates a block of atactic propylene. As the ligands rotate, the catalyst produces alternating blocks of isotactic and atactic polymer, much like a miniature sewing machine switched back and forth between two different kinds of stitches.

One further trick is required to make the machine work. Indenyl ligands rotate so much faster than the polymerization reaction that stereoregular polymer blocks don't form. To overcome this, Waymouth and Coates add a phenyl substituent to the ligand to slow down the rate of rotation—so that it is slower than that of monomer insertion yet faster than the time required to construct a complete polymer chain. Thus, several monomers are incorporated into the growing polymer chain before the switch is thrown to produce the al nate block type.

The specific compound Waymou and Coates synthesize is bis(2-pher indenyl) zirconium—which is abbre ated as $(2\text{-PhInd})_2ZrCl_2$. They der their catalyst from $(2\text{-PhInd})_2ZrCl_2$ a methylaluminoxane.

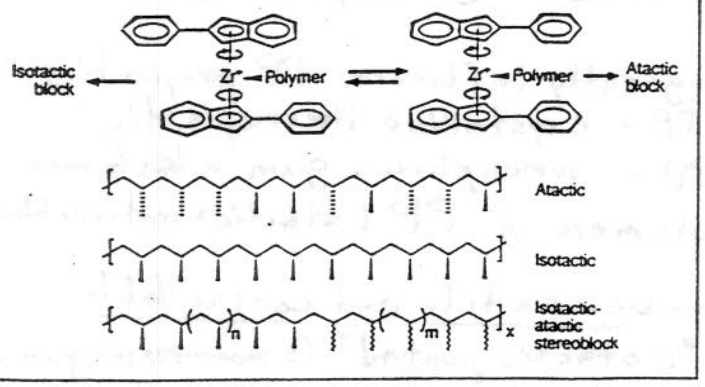
"One of the most remarkable a powerful attributes of this catalyst s tem is the sensitivity of the polymer r crostructure to the reaction condition Waymouth stresses. As monomer pr sure is increased, the isotacticity of t polypropylene also increases—behav that is consistent with the polymeri tion mechanism the catalyst was c signed to follow.

The microstructure of polypropyle is commonly described in terms of t "isotactic pentad content," which is t fraction of stereosequences containi five adjacent isotactic stereocenters. I varying reaction conditions, Waymou says, the new catalyst produces polypr pylenes with isotactic pentads rangi from 6.3 to 28.1%.

"Other researchers have made ru bery polypropylene," he adds. "But b cause we are beginning to understar how our catalyst works, we can contr the properties of the polypropy a huge range. We can produce n that can be stretched to eight times length and snaps back, or we can ma material that is very stiff and hard."

Rudy Bau

Oscillating catalyst produces stereoblock polymers



Altered bacteria make ethanol from xylose

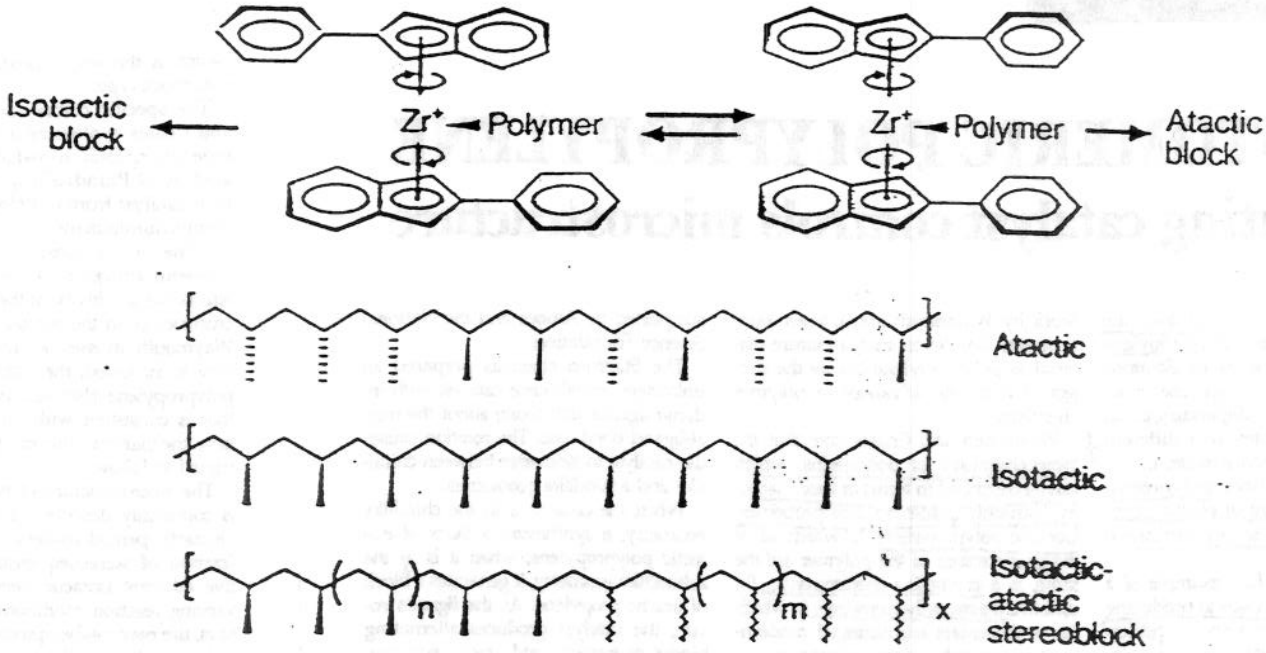
Researchers have achieved a key step efforts to develop genetically engineere bacteria that can produce ethanol ef ciently from plant biomass for use in a ternative transportation fuels.

Scientists at the Department of Ene gy's National Renewable Energy Lab ratory (NREL) in Golden, Colo., ha genetically modified the bacterium Z *momonas mobilis*—whose natural for produces ethanol from the six-carbo (hexose) sugars glucose and fructo and the disaccharide sucrose—so that also makes ethanol from the fiv carbon (pentose) sugar xylose.

Glucose and xylose are major brea down products of the cellulose an hemicellulose that make up two-thir to three-fourths of plant biomass.

ELASTOMERIC POLYPROPYLENE

Oscillating catalyst produces stereoblock polymers



C&EN NEWS, Jan. 16, 1995

1) Uniqueness of system:
- block copolymers (Atactic and isotactic stereoblocks) achieved not by changing monomer, but by polymerizing the same monomer in a different way.

2) Product: Elastomeric polypropylene
- thermoplastic (recyclable)

3) Stereochemistry greatly influences PP properties
- isotactic PP – crystalline thermoplastic
- Atactic PP – amorphous gum elastomer
- block copolymer of PP (Atactic + isotactic blocks) – rubbery

4) Catalyst system <u>versatile</u> and <u>controllable</u>.
- can control "isotactic pentad" (5 monomers in sequence) from 6.3% – 28.1%

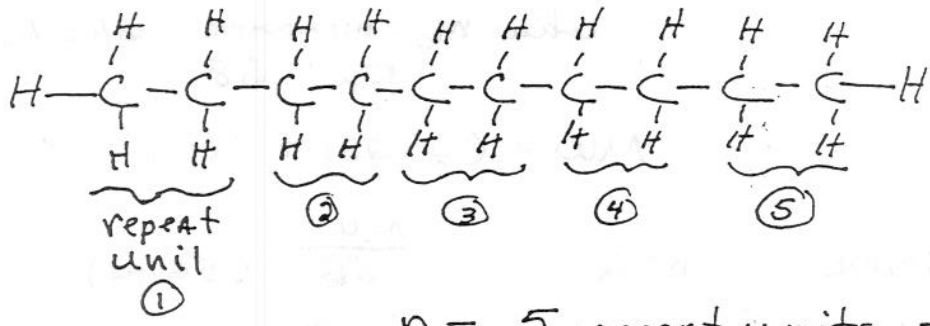
(5) Interesting and varied PP properties obtainable
- very elastic material – stretch 8 times Lo and <u>snap</u> back
- crystalline material – stiff and hard.

How does one make a polymer?

Example: Polyethylene (PE)

monomer: ethylene $CH_2=CH_2$

polymerization: $CH_2=CH_2 \xrightarrow[\text{high P}]{\text{high T}} \left[CH_2-CH_2\right]_n$



n = 5 repeat units = <u>pentamer</u>

n = 2 repeat units dimer

n = 3 repeat units trimer

⋮ etc.

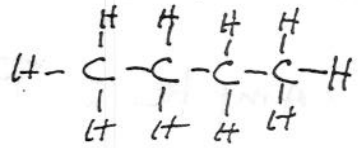
- n = 3 – 50 repeat units <u>oligomer</u> (pre-polym
- n ≥ 100 repeat units <u>polymer</u>.

shorthand notation $\left[CH_2-CH_2\right]_n$

where n = # repeat units

Molecular Weight Concept.

PE $n = 2$ (dimer)



Molecular weight (MW) $= (4 \times 12) + 10(1) = 58$

$MW = (2 \times m_o) +$ end groups

where m_o = monomer molecular weight

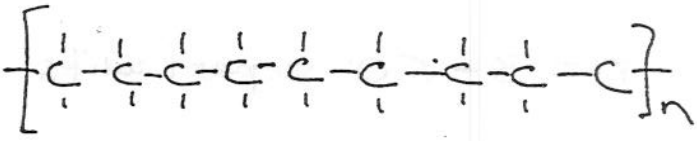
$m_o = 28$

$MW = (2 \times 28) + 2(1) = 58$

		MW	
dimer	$n = 2$	58	(56 + 2)
pentamer	$n = 5$	142	(140 + 2)
polymer	$n \geq 100$	28,000	
typical commercial polymer	$n > 1000$	280,000 *	

* About minimum value for commercial product.

Question.



Why is this polyethylene and not polymethylene?

Why is $n = 5$ pentamer and not $n = 10$?

Because basic unit for synthesis of PE is

$[CH_2 = CH_2]$ not $[CH_4]$

∴ ethylene methane.

Polymer Molecular Weight

$$\bar{D}_n = \frac{\Sigma\, n_i D_i}{\Sigma\, n_i}$$

$$\bar{D}_w = \frac{\Sigma\, w_i D_i}{\Sigma\, w_i}$$

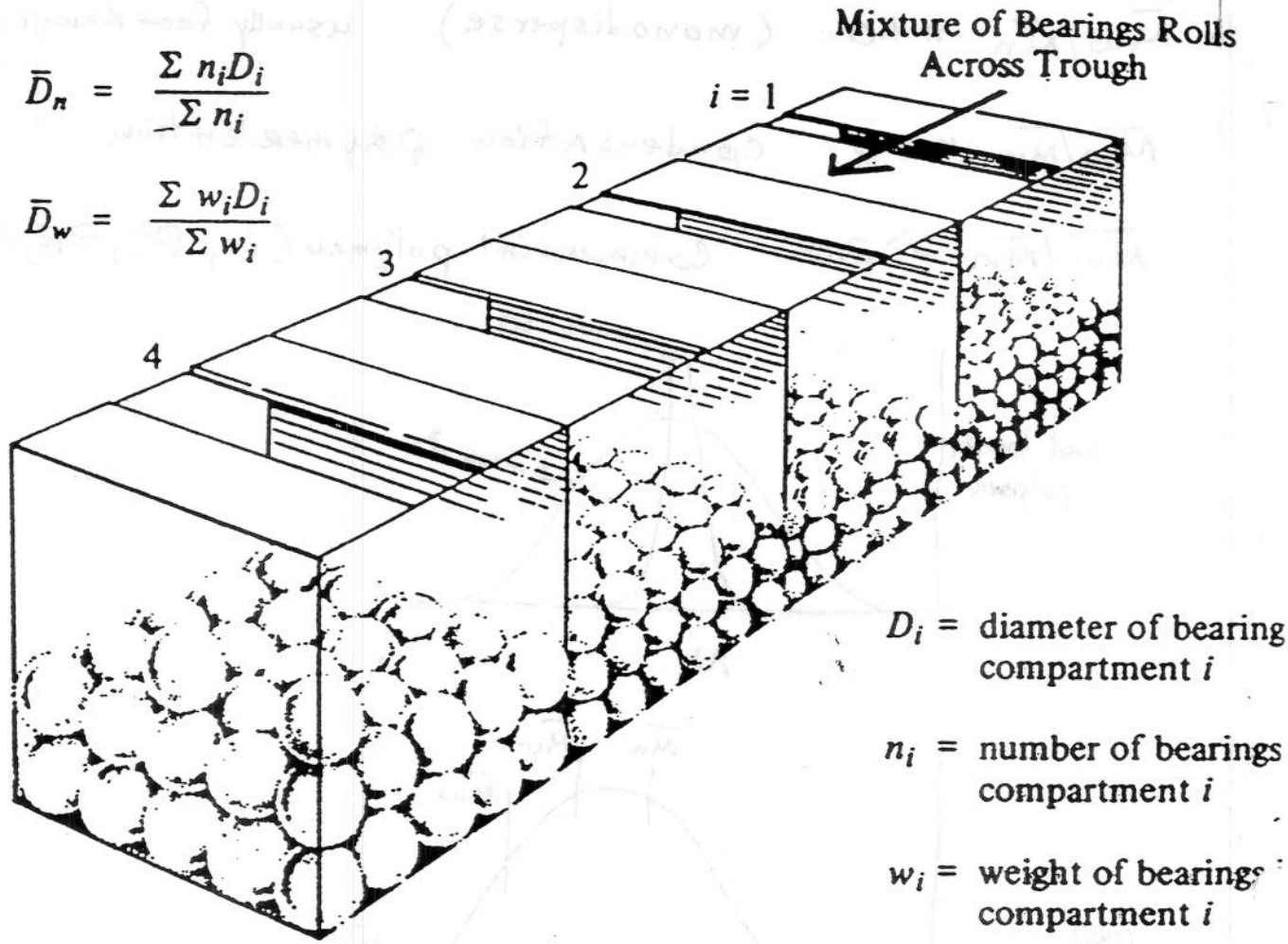


Figure 6.1 Ball bearing analogy for average molecular weights

$$M = w/n = \frac{\text{total sample weight.}}{\text{\# moles in sample}} \Leftrightarrow \frac{\text{mass}}{\text{mole}} = \text{Daltons}$$

Number Average Molecular Weight ($\bar{M}_n$):

$$\bar{M}_n = \frac{w}{n} = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

n_i = # moles of i-mers
M_i = Molecular Weight of i-mer

Weight Average Molecular Weight ($\bar{M}_w$):

$$\bar{M}_w = \frac{\sum_i w_i M_i}{\sum_i w_i} = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$$

($w_i = n_i M_i$ = wgt of i-m

Z-Average Molecular Weight ($\bar{M}_z$):

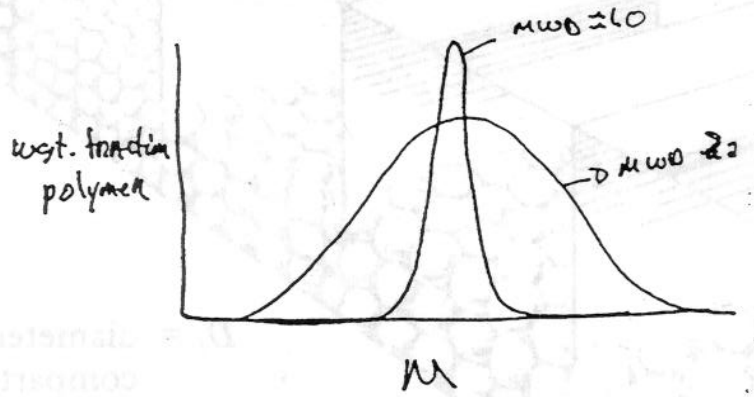
$$\bar{M}_z = \sum_i n_i M_i^3 \Big/ \sum_i n_i M_i^2 \quad \text{(third moment)}$$

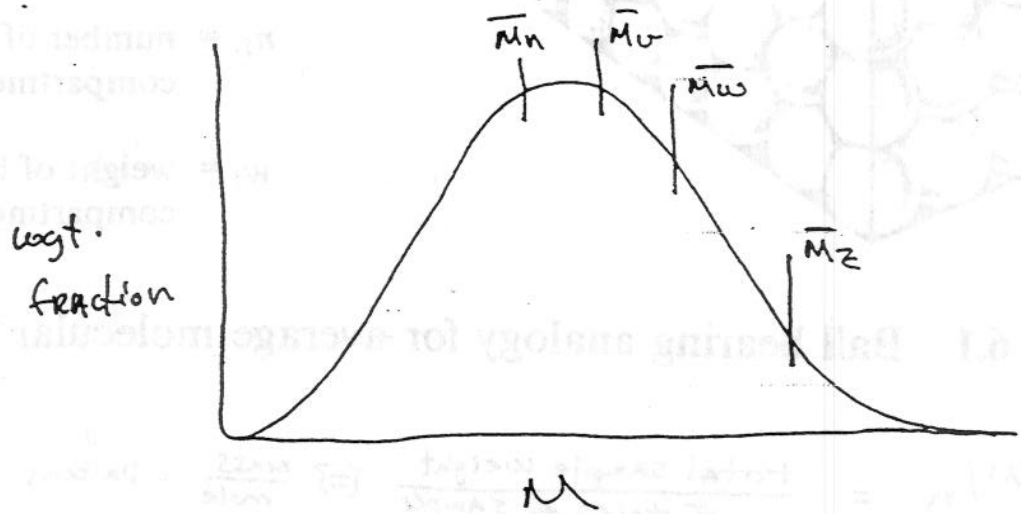
Molecular Weight Distribution (MWD)

$\bar{M}_w/\bar{M}_n \approx 1.0$ (monodisperse) usually from anionic polymers

$\bar{M}_w/\bar{M}_n \approx 2.0$ condensation polymerization.

$\bar{M}_w/\bar{M}_n >> 2.0$ commercial polymers (i.e, PS, PE, PP)





Typical Values of Mol Wgt. and MWD

	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_v$	$\bar{M}_w/\bar{M}_n$
Polystyrene	$\sim 1.0\times10^5$	2×10^5	1.75×10^5	2.0
HDPE	1.75×10^4	3.0×10^5	2.9×10^5	17.5
Linear LDPE	2×10^4	1.45×10^5	7.8×10^4	7.25