

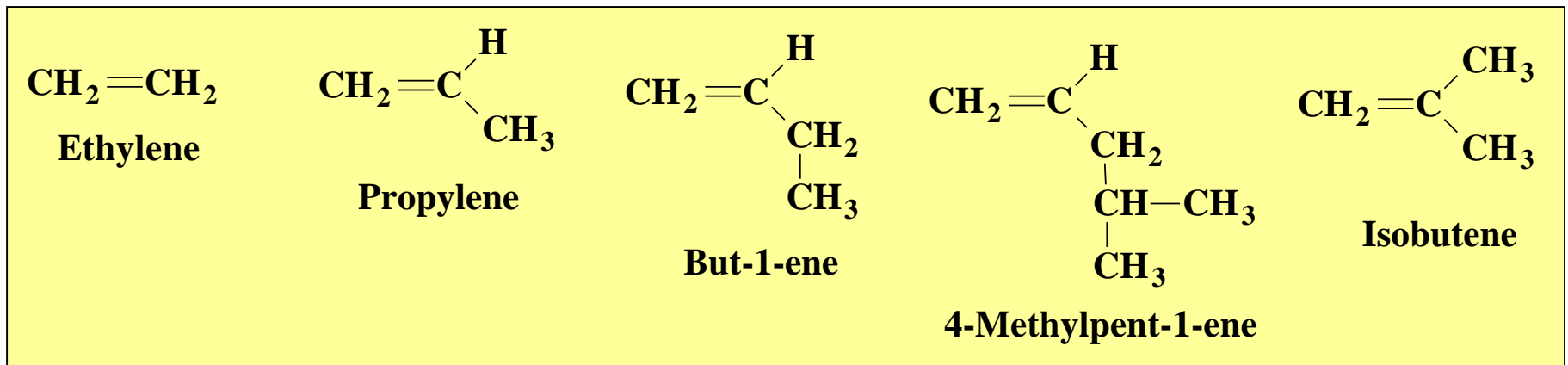
Topics to be Covered

- *Elements of Addition Polymerization*
- *Branching and Tacticity*
- *The Effect of Crystallinity on Properties*

Chapters 1 & 2 in CD (Polymer Science and Engineering)

What Are Polyolefins?

The term polyolefin embraces all polymers that are derived from simple unsaturated aliphatic hydrocarbons that contain one double bond per monomer. Examples include:



The most important polyolefins in terms of production volume are polyethylene (PE), polypropylene (PP) and the ethylene/propylene copolymers (EP). Other significant polyolefins include, polybut-1-ene, poly-4-methylpent-1-ene and polyisobutene (PIB).

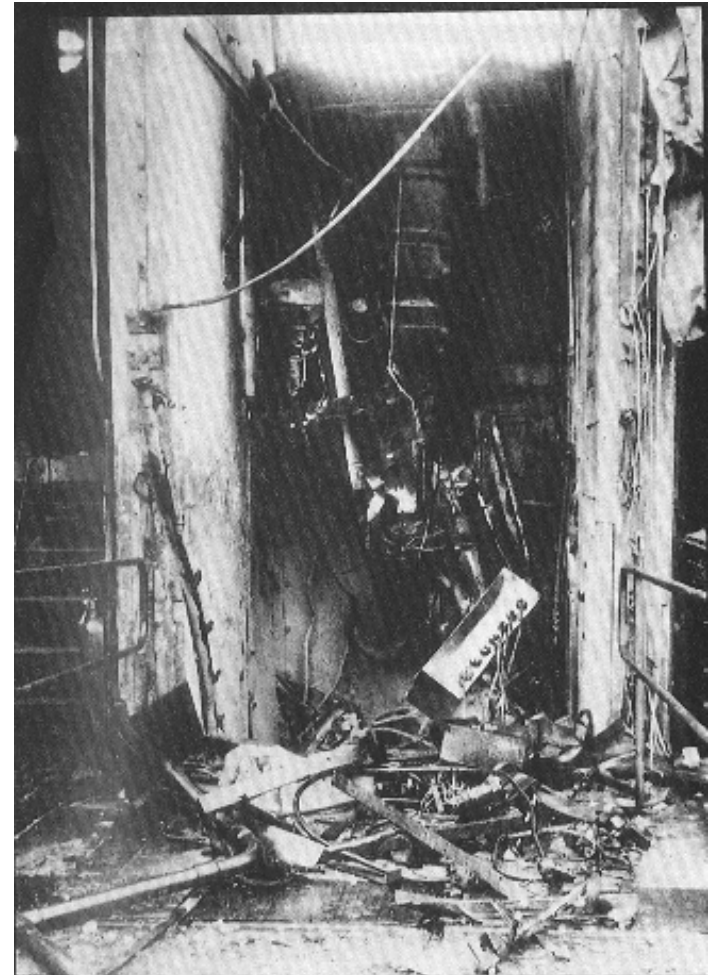
Low Density Polyethylene

~ 1890's

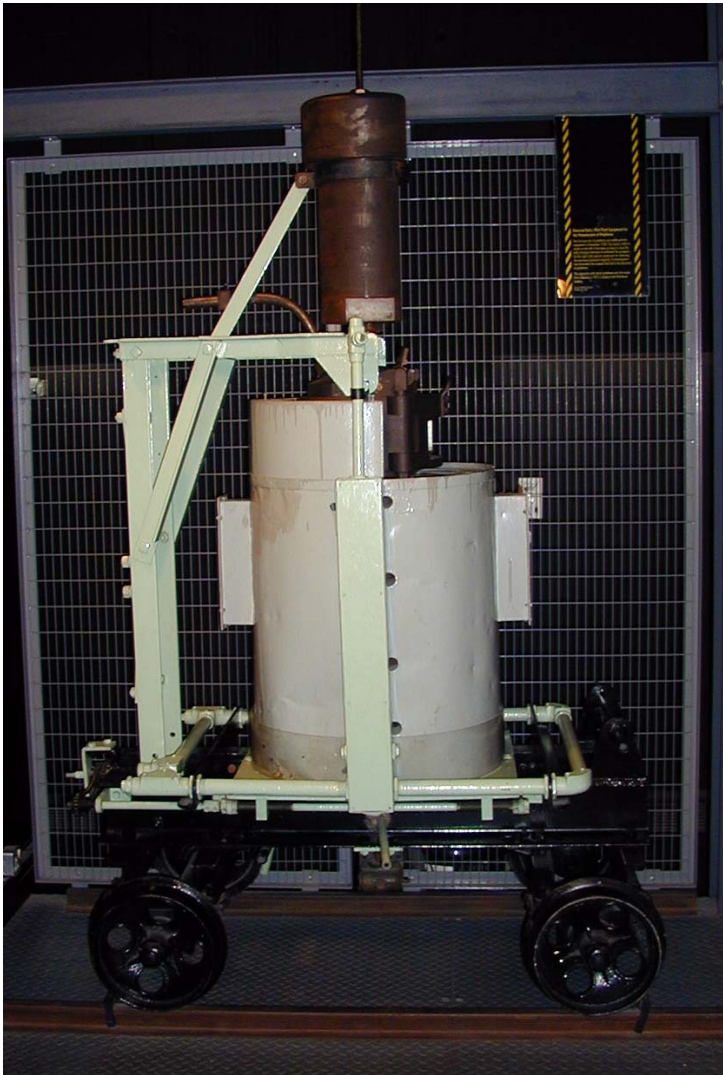


~ 1930's

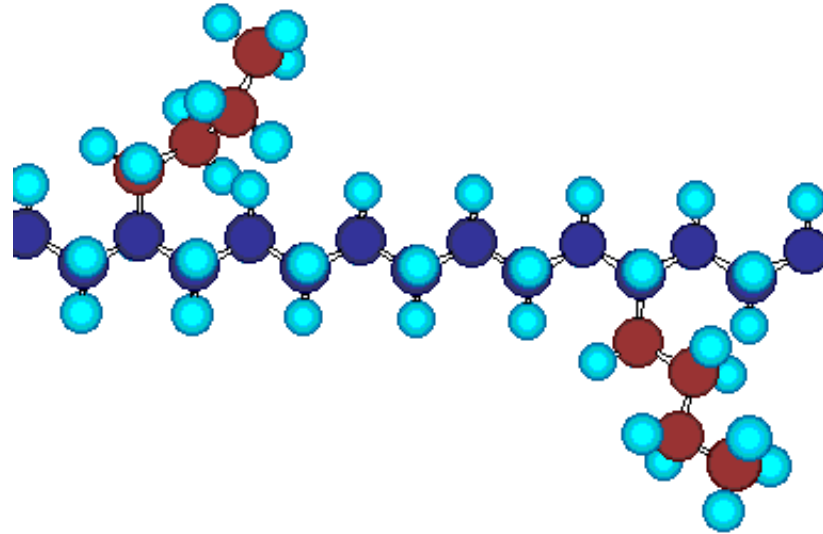
ICI - chemical reactions under pressure; Ethylene + Benzaldehyde



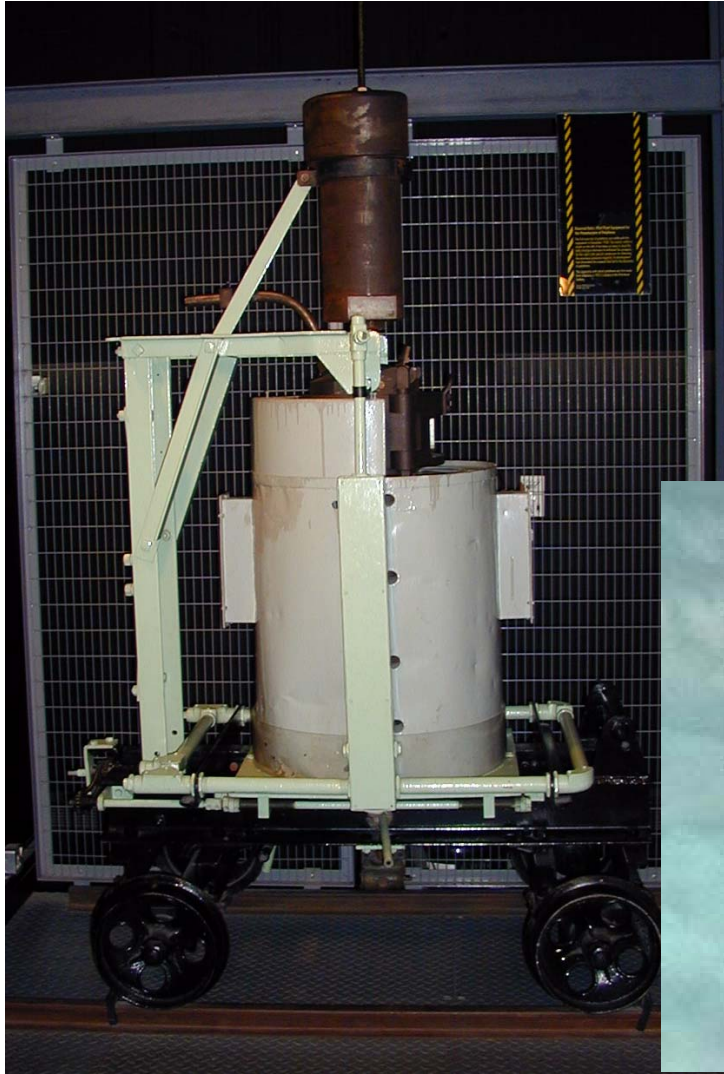
Low Density Polyethylene



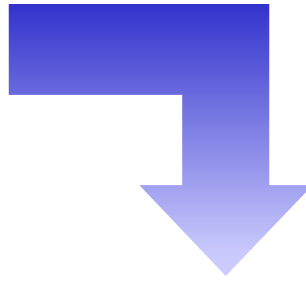
The original ICI pilot plant



A modern cable coating



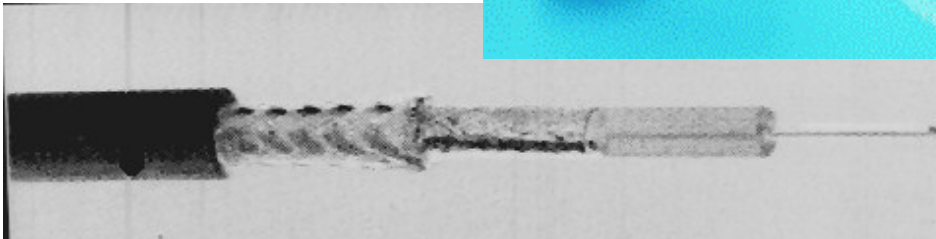
This allowed



this to triumph



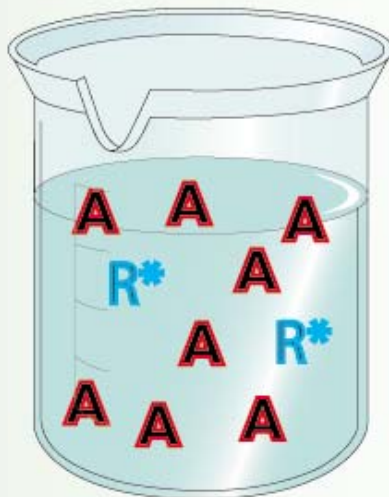
Low Density Polyethylene



Chain Polymerizations

Monomers

One type of reactive monomer $A + R^*$

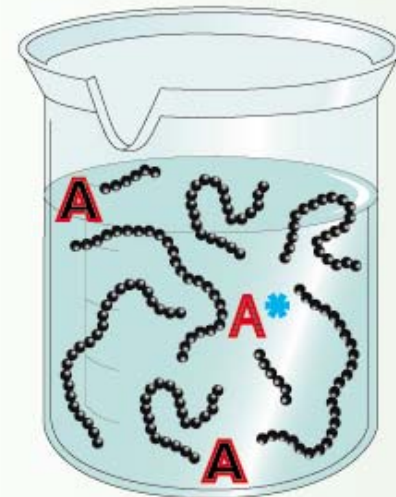


FAST



Polymer

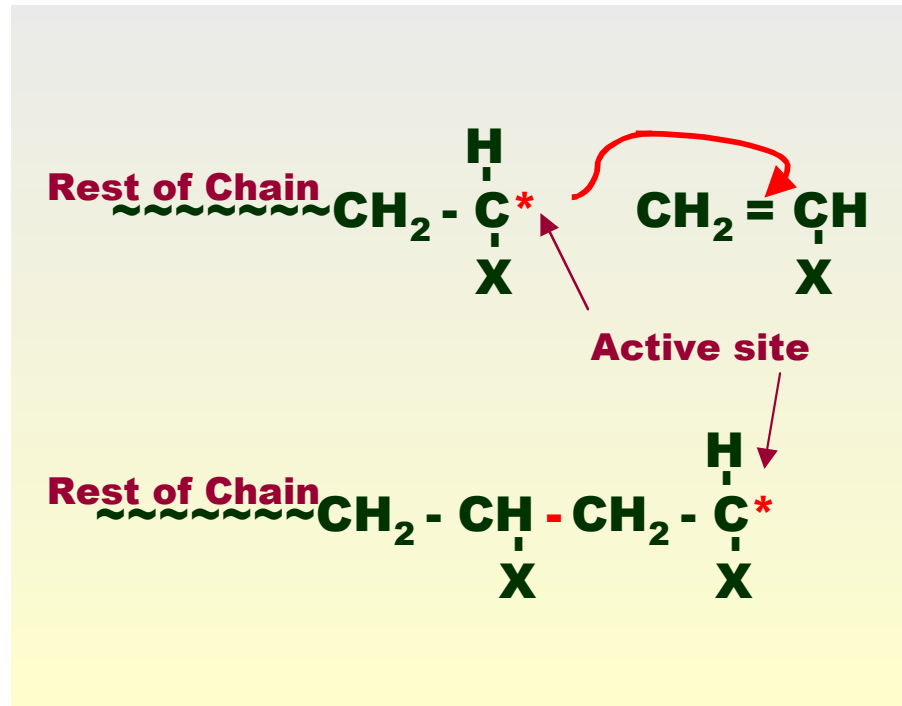
Plus residual monomer A and very small amount of growing chains A^*



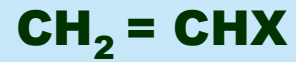
Characteristics of Chain Polymerizations

Need to consider;

- 1. Initiation*
- 2. Propagation*
- 3. Termination*
- 4. Chain Transfer*



Chain Polymerizations



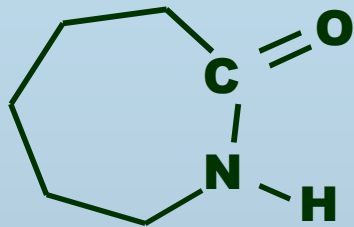
Various Olefins and Vinyl Monomers



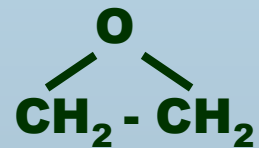
Various Dienes



Acetylene



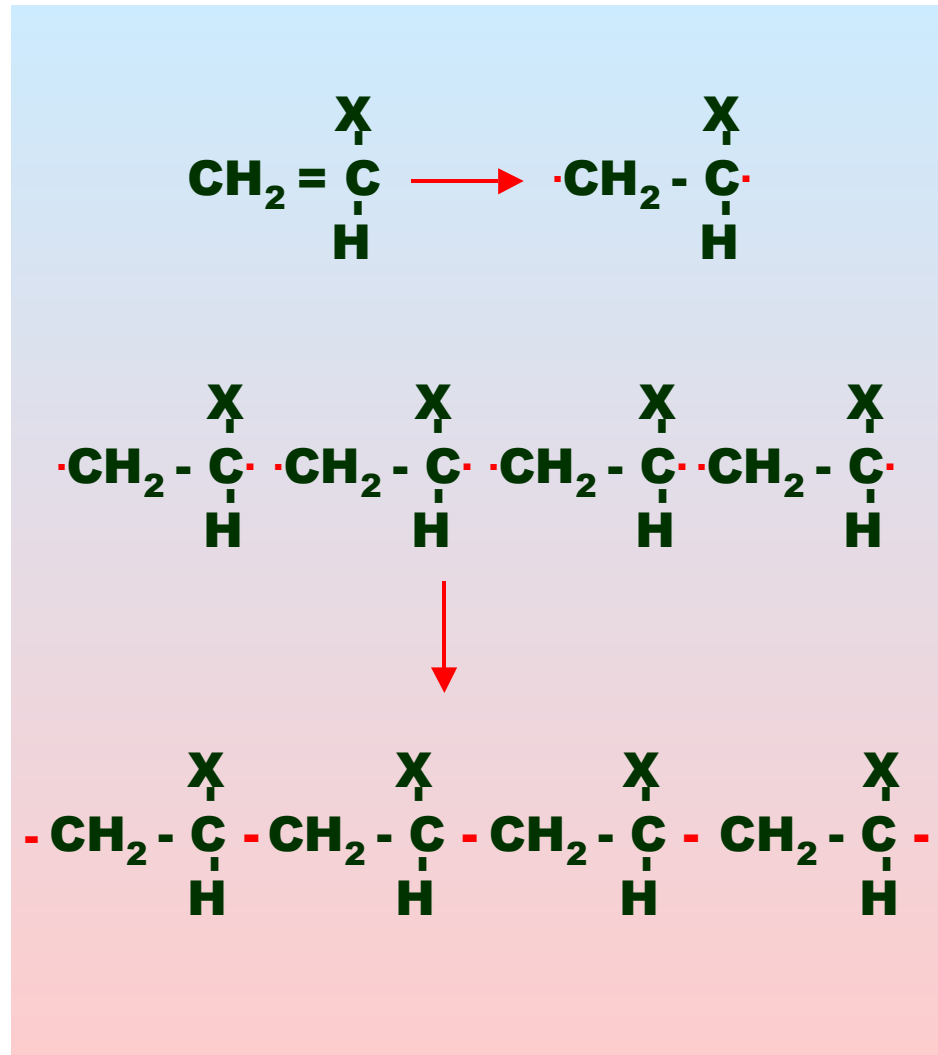
Caprolactam



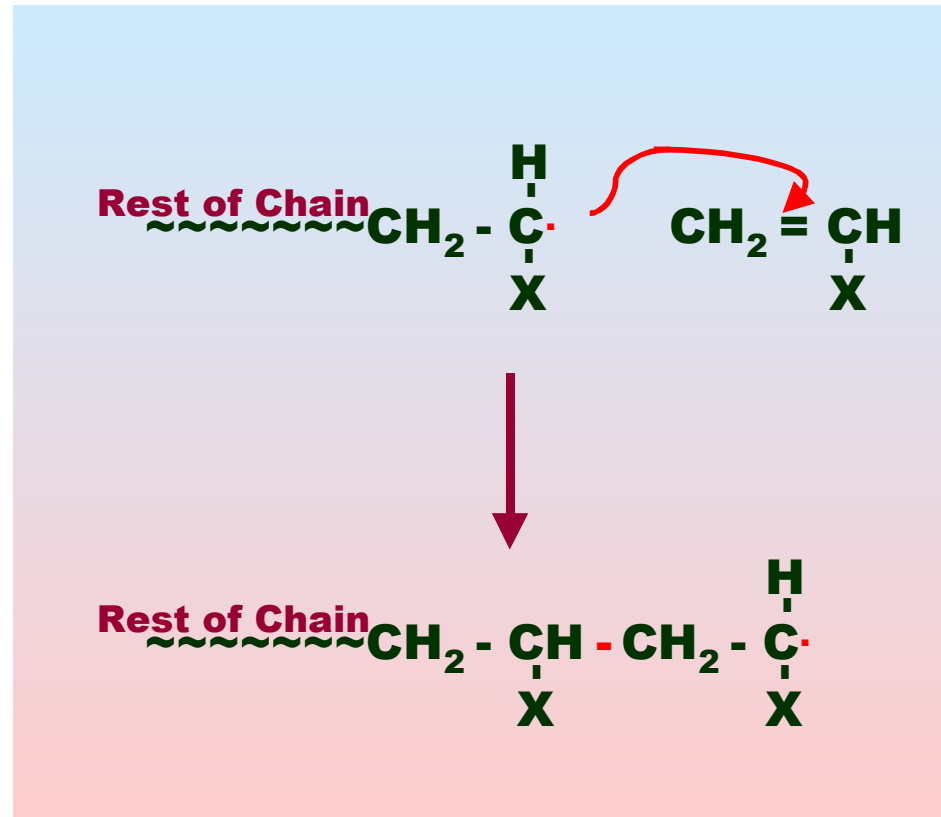
Ethylene Oxide

Chain Polymerizations

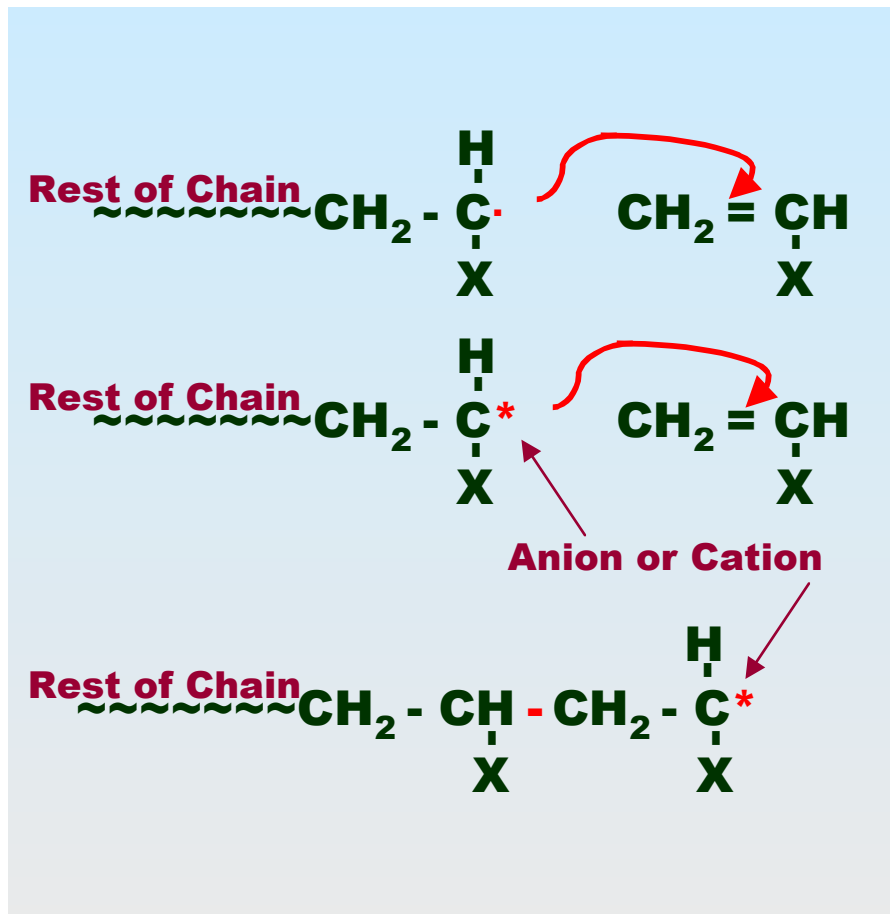
- a simplistic view



Chain Polymerizations



Chain Polymerizations – Types (nature of the active site)



Free Radical

Anionic

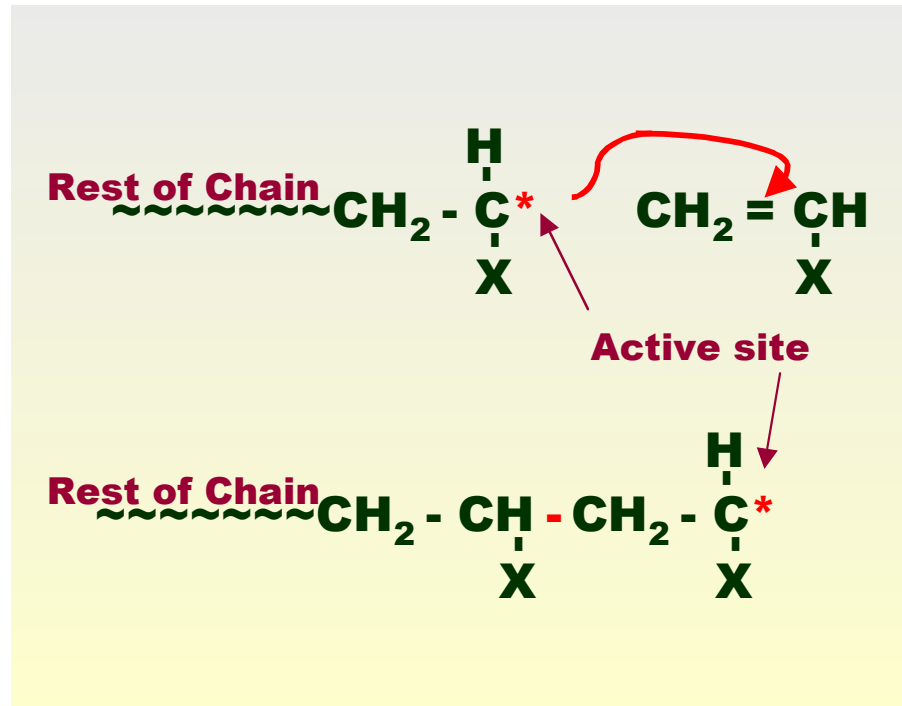
Cationic

Coordination (Catalyst)

Characteristics of Chain Polymerizations

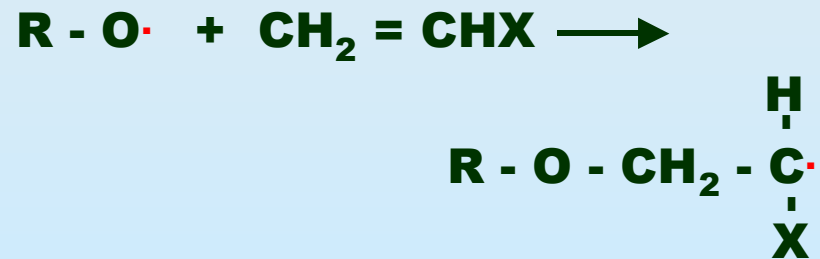
Need to consider;

- 1. Initiation*
- 2. Propagation*
- 3. Termination*
- 4. Chain Transfer*

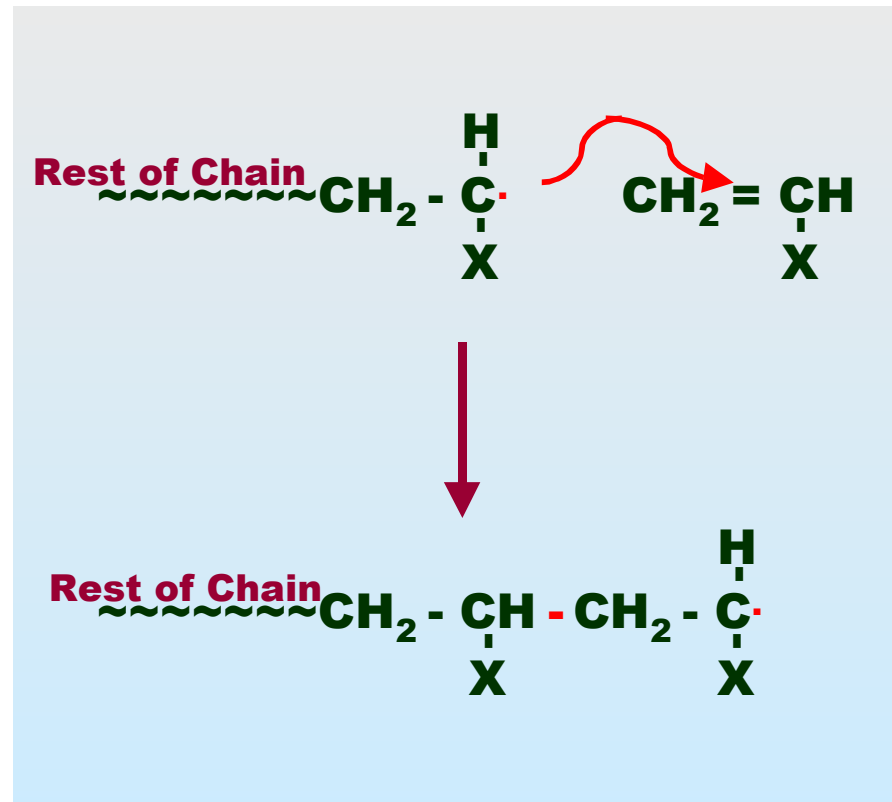


Free Radical Polymerization - Initiation

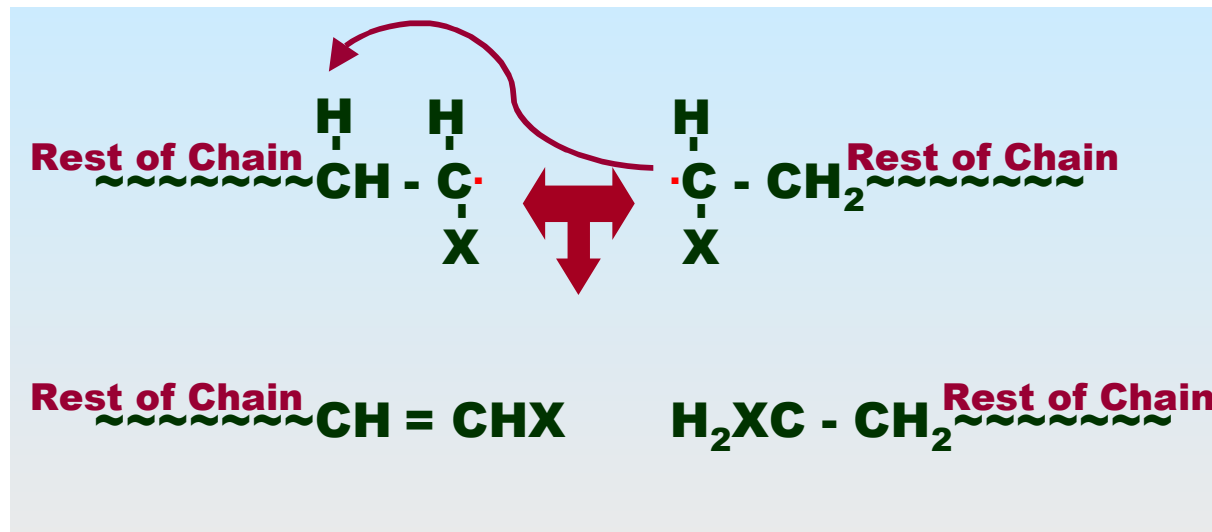
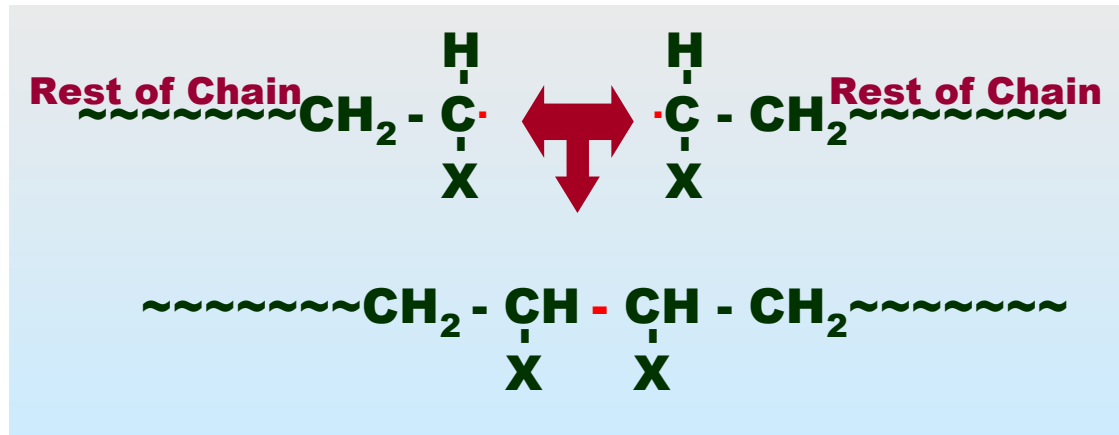
INITIATION



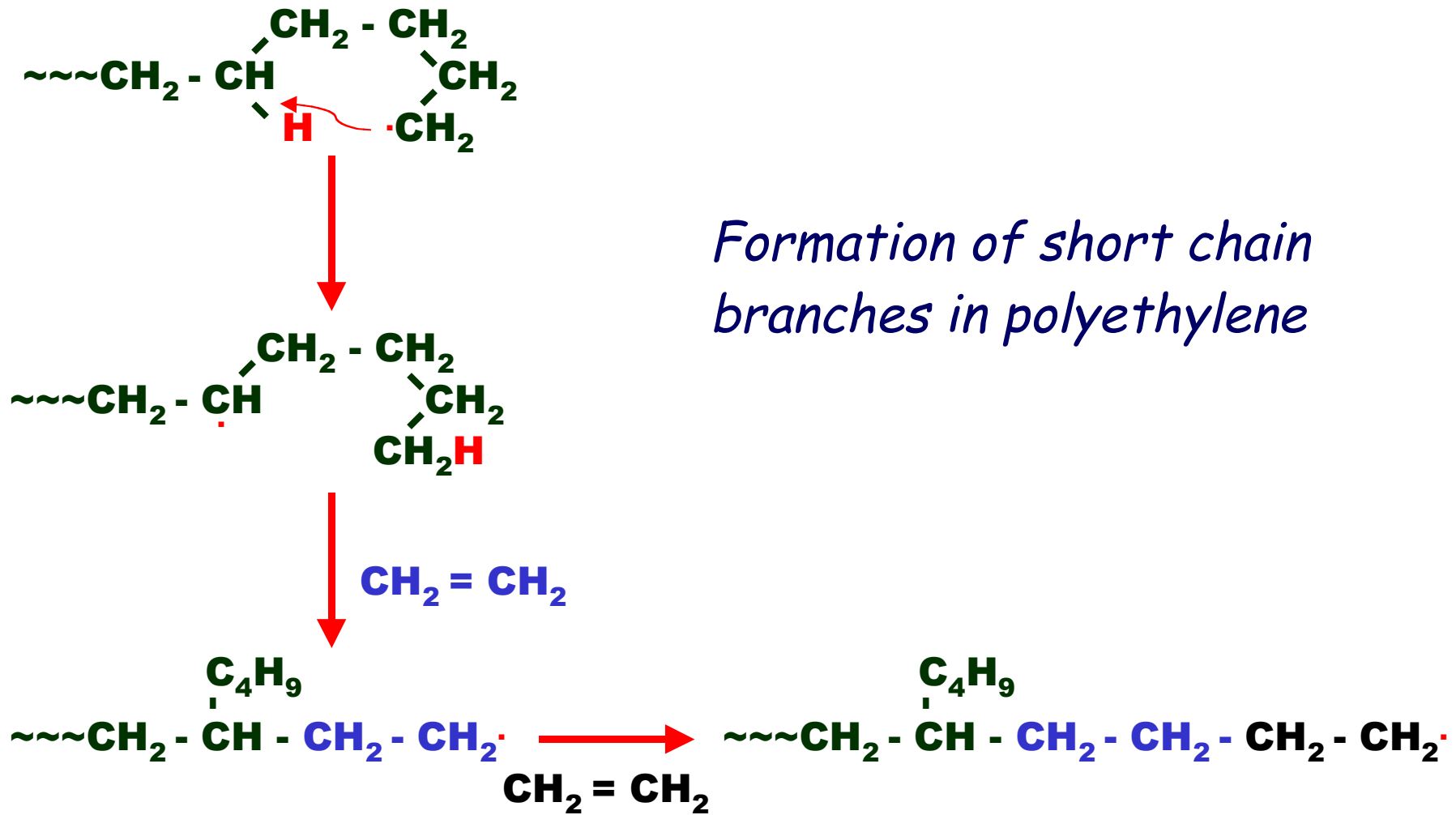
Free Radical Polymerization - Propagation



Free Radical Polymerization - Termination

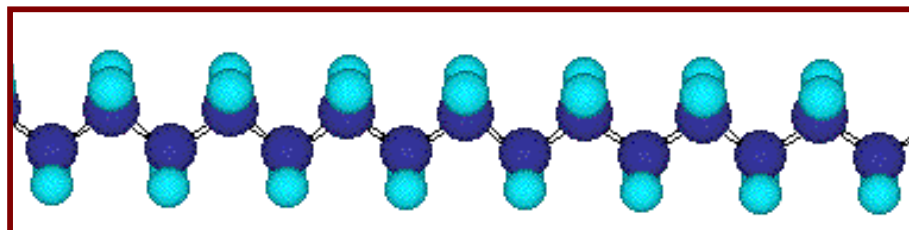


Short Chain Branching in Polyethylene

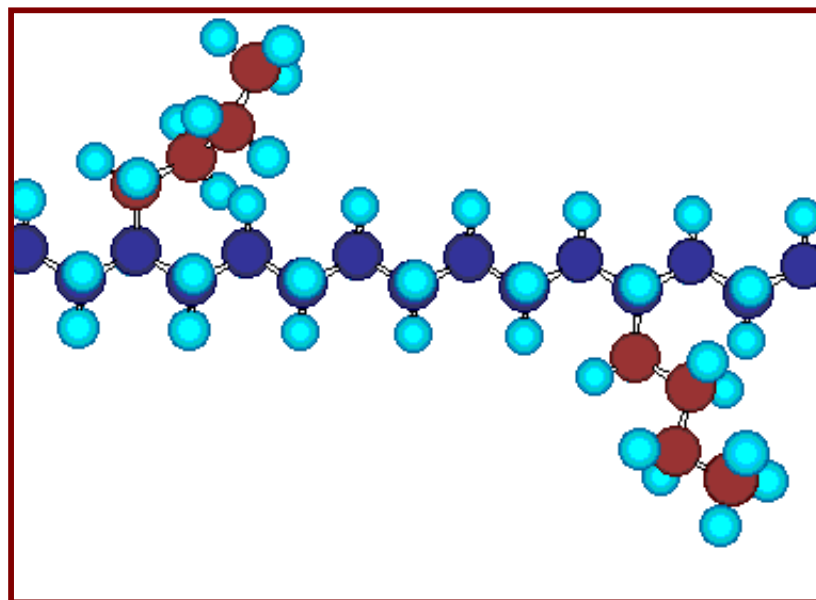


Linear and Branched Polymers

Linear

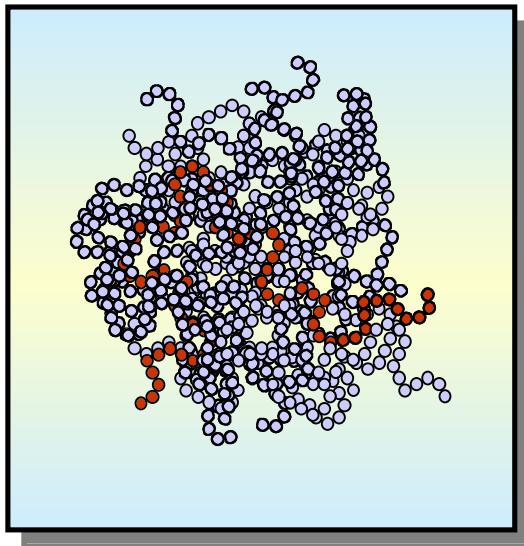


Branched



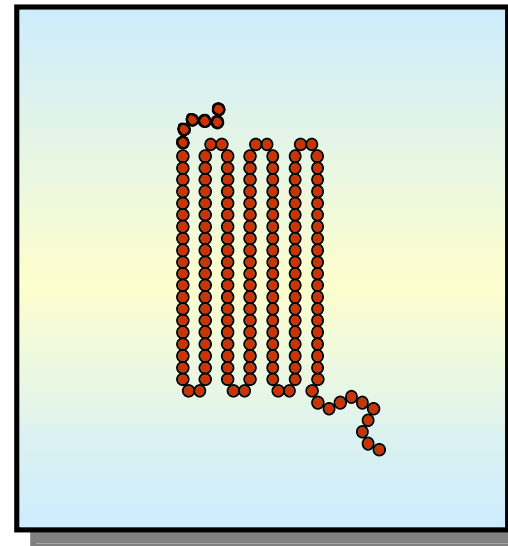
Crystallinity in Polymers

Let's establish a simple connection between structure and properties right from the beginning. We'll explore polymer morphology in more detail later, but simplistically we can get:



RANDOM COILS

Like “cooked spaghetti”



SEMICRYSTALLINE POLYMERS

A bit like “uncooked spaghetti”

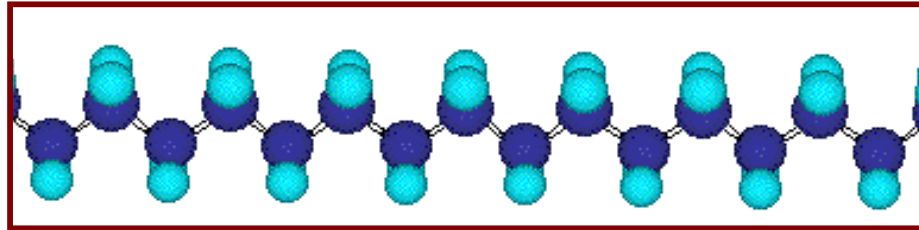
The Effect of Crystallinity on Properties

We will be asking how crystallinity affects

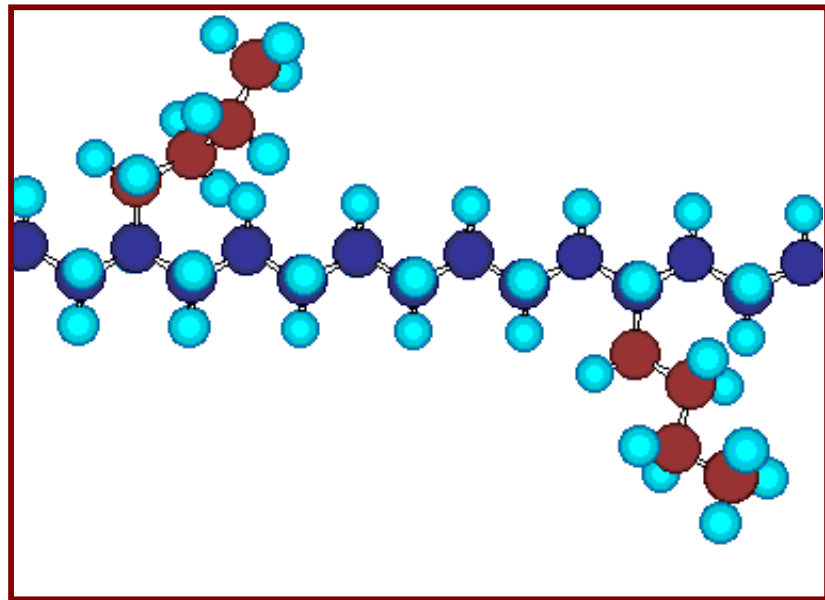
- Strength
- Stiffness
- Toughness
- Barrier Properties
- Solubility
- Transparency
- Thermal Properties
- Etc

Linear and Branched Polymers

Linear

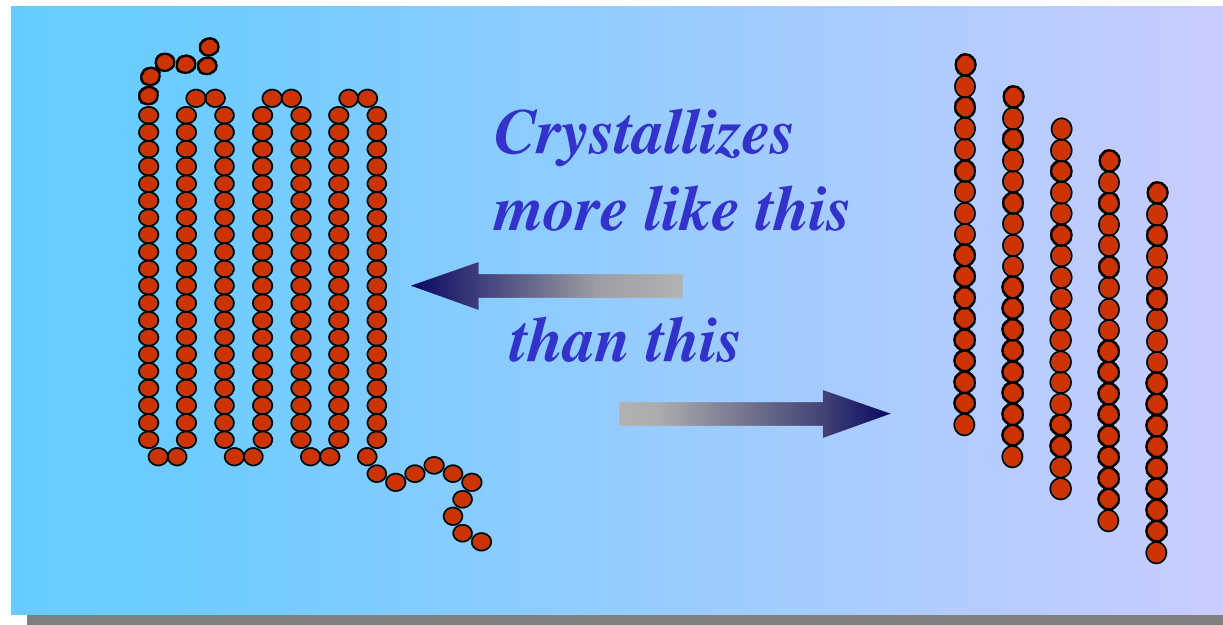


Branched



Which of these is more likely to crystallize?

The answer is *linear* !



Various grades of polyethylene are produced commercially and are often referred to as "high density" or "low density". Which do you think is the high density polyethylene

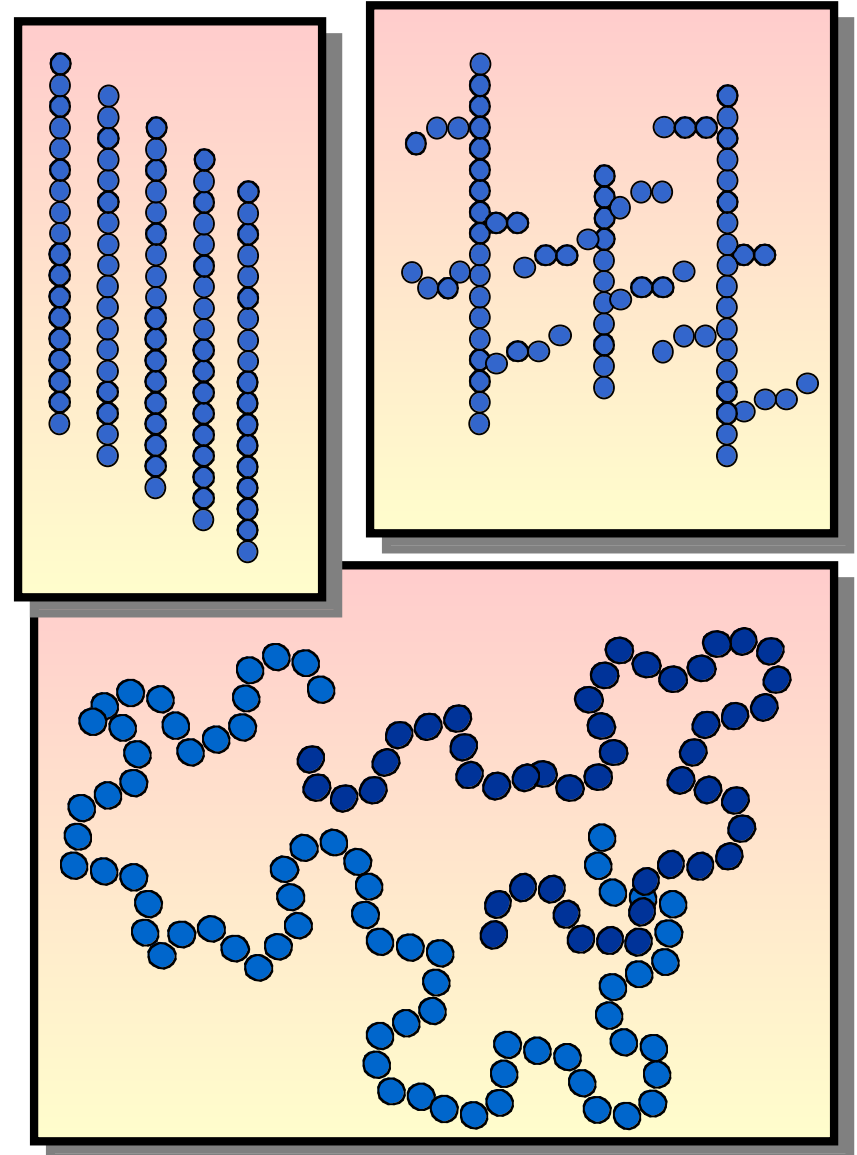
- A. *The linear, more crystalline stuff ?*
- B. *The (somewhat) branched less crystalline stuff ?*

The answer is still *linear* !

Chains that cannot crystallize (e.g., highly branched ones), or even linear chains that are heated above their crystalline melting points, actually look something like cooked spaghetti or random coils.



They do not pack as closely together as in the crystalline state.



The Effect of Crystallinity on Properties

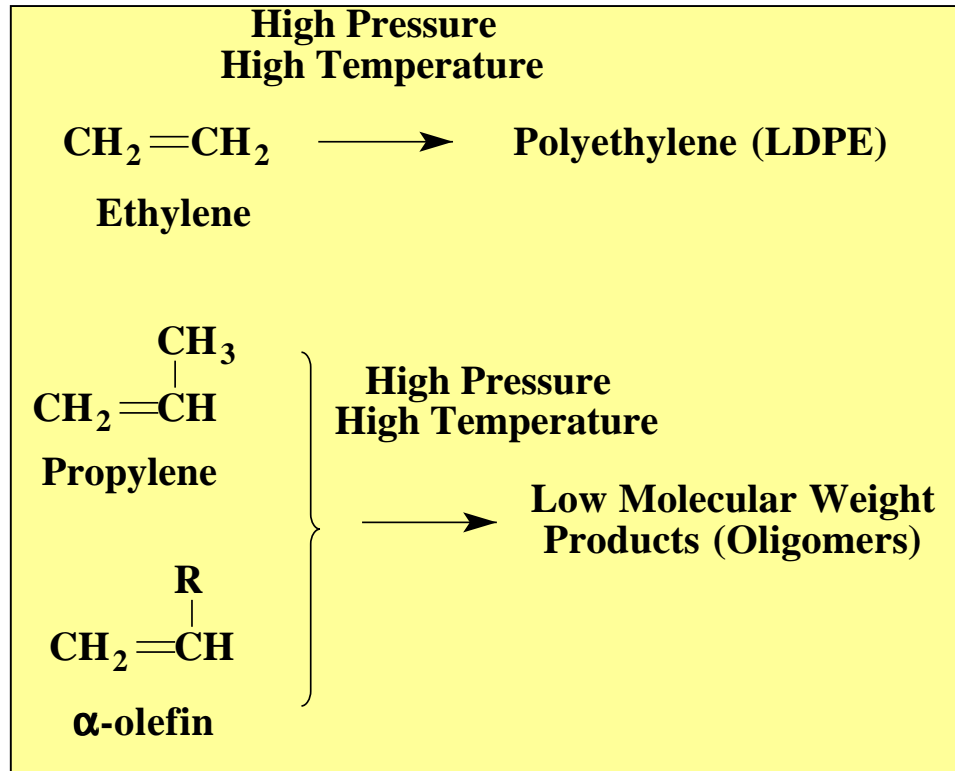
The type of polyethylene that goes into milk jugs is stronger, stiffer, but more opaque (less optically clear) than the type of polyethylene that is used to make film wrap (greater optical clarity, more flexible, but less strong). Can you figure out which type of polyethylene is used to make film wrap?

- A. High density
- B. Low density



Property	Change with Increasing Degree of Crystallinity
Strength	Generally increases with degree of crystallinity
Stiffness	Generally increases with degree of crystallinity
Toughness	Generally decreases with degree of crystallinity
Optical Clarity	Generally decreases with increasing degree of crystallinity. Semi-crystalline polymers usually appear opaque because of the difference in refractive index of the amorphous and crystalline domains, which leads to scattering. Will depend upon crystallite size.
Barrier Properties	Small molecules usually cannot penetrate or diffuse through the crystalline domains, hence "barrier properties", which make a polymer useful for things like food wrap, increase with degree of crystallinity
Solubility	Similarly, solvent molecules cannot penetrate the crystalline domains, which must be melted before the polymer will dissolve. Solvent resistance increases with degree of crystallinity

What is the Problem with Propylene?



First - The Metal Oxide Catalysts and Linear Polyethylene



Hogan and Banks synthesized polypropylene and linear polyethylene in a low pressure process using metal oxide catalysts.

“A Company Maker”

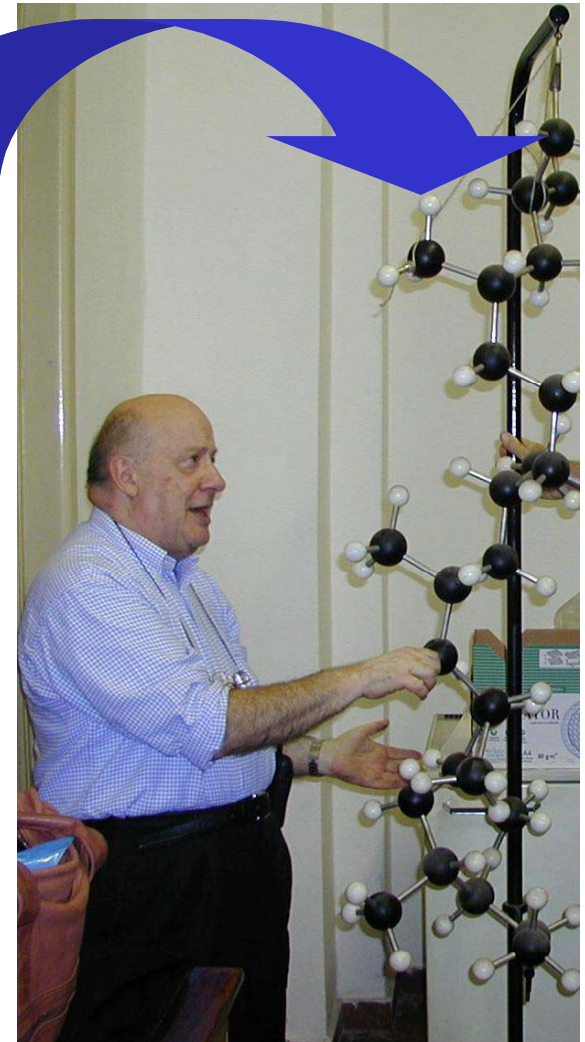
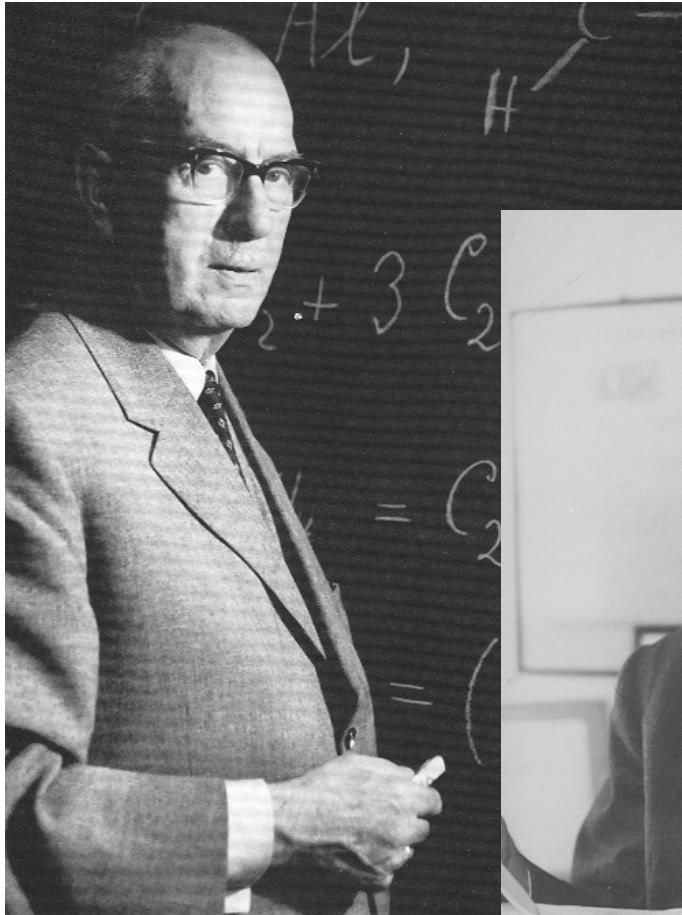


The Hula Hoop!

*The French can make even
polyethylene look sexy!*

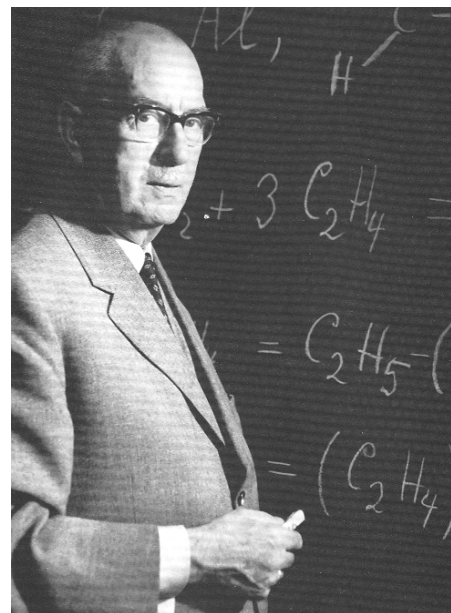


Ziegler and Natta



Ziegler and the Organometallic Catalysts

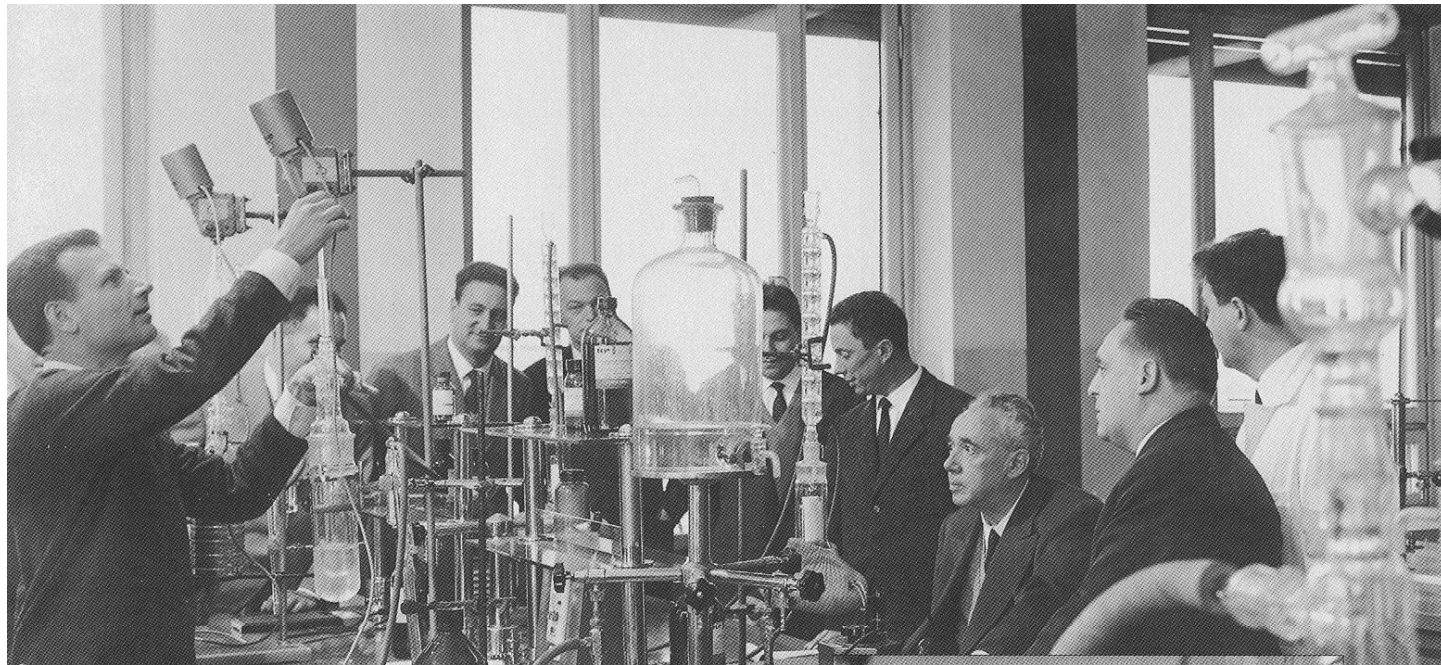
In his lecture at the Nobel Prize award ceremony, Ziegler described his preliminary work thus, “*The development began at the end of 1953 when Holzkamp, Breil, Martin and myself, in a few almost dramatic days, observed that the gas ethylene could be polymerized at 100, 20, or 5 atmospheres and finally even at atmospheric pressure very rapidly in the presence of certain, easily prepared, catalysts to give a high molecular weight plastic.*”



	<i>High Pressure Polyethylene</i>	<i>Ziegler Polyethylene</i>	<i>Metal Oxide Polyethylene</i>
<i>Molecular Weight (Mn)</i>	<i>20000</i>	<i>15000</i>	<i>15000</i>
<i>Number of Me groups/1000 Carbons</i>	<i>30</i>	<i>6</i>	<i>< 0.15</i>
<i>Density (g/cc)</i>	<i>0.92</i>	<i>0.95</i>	<i>0.96</i>
<i>Crystalline Melting Point (°C)</i>	<i>108</i>	<i>130</i>	<i>133</i>

Natta and Stereoregularity

In the middle of 1954, Natta and his coworkers, having been informed by Ziegler of the nature of his original HDPE catalyst, used it to polymerize propylene and obtained a partially “crystalline”, essentially *isotactic*, polypropylene (more on this shortly). Subsequently, Natta and his coworkers made changes to the catalyst, replacing TiCl_4 with TiCl_3 , which increased the isotacticity of polypropylene from 50-70 to 80-90%.



Into Court!

Natta's research in this area was funded by the Italian company Montecatini and a patent was filed jointly soon thereafter. Unfortunately, this caused considerable 'bad blood' between Ziegler and Natta and resulted in one of the longest lasting patent cases of all time.





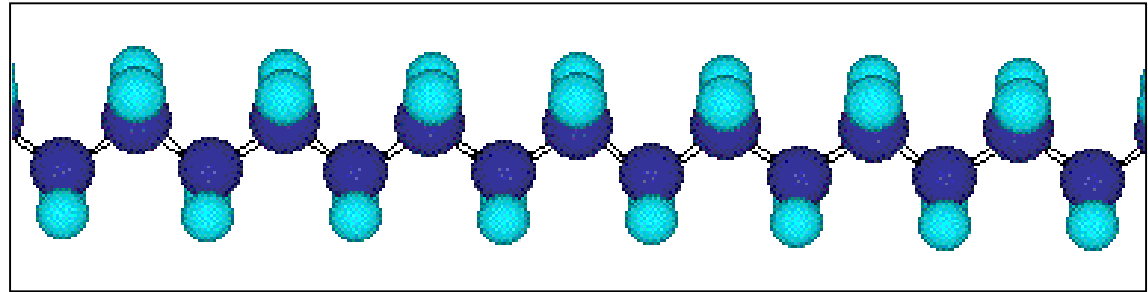


The Many Uses of Polypropylene

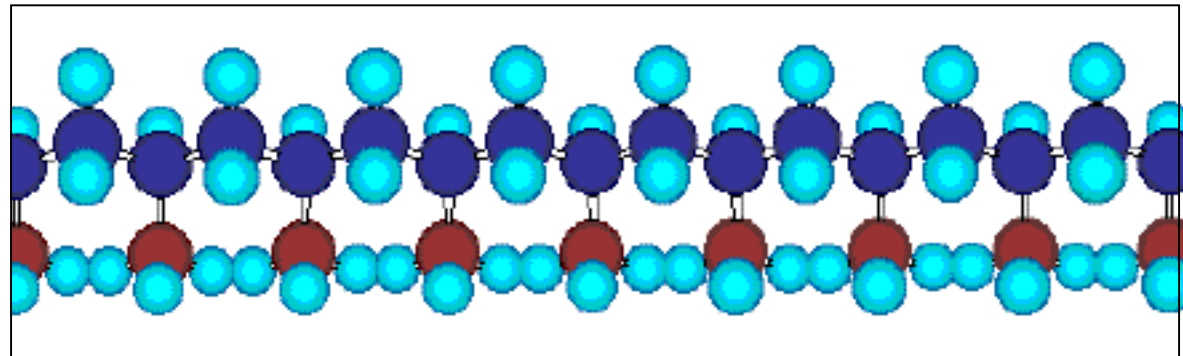


Summary

1950 - 1953

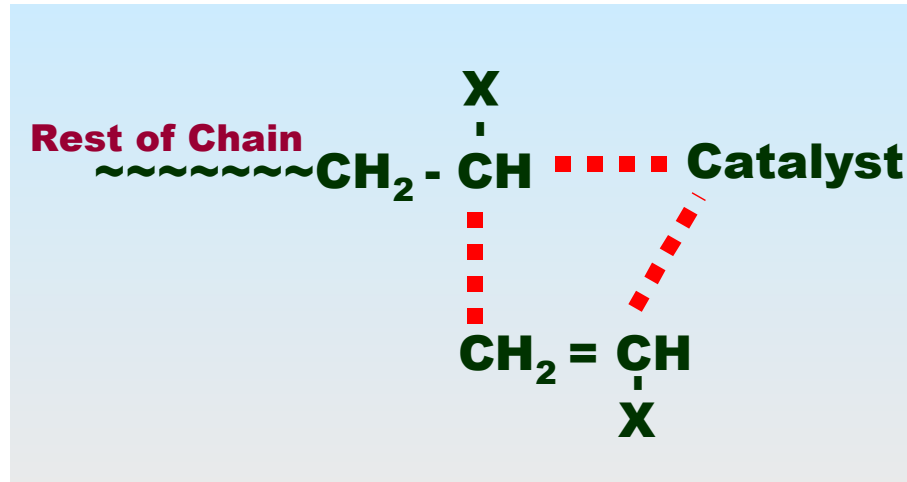


Ziegler-Natta Catalysts
Metal Oxide Catalysts



Linear PE and stereoregular polyolefins

Coordination Polymerization



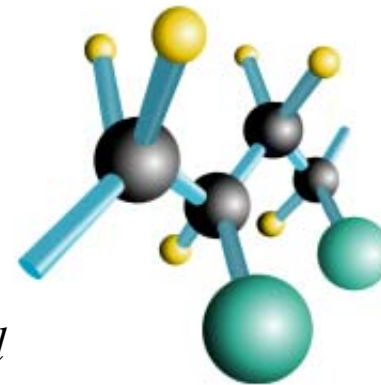
Isomerism in Polymers

- Sequence isomerism
- *Stereoisomerism (in vinyl polymers)*
- Structural isomerism (in diene polymers)

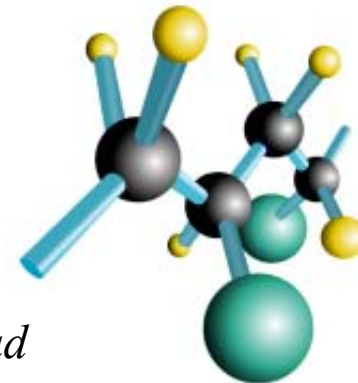
Two molecules are said to be isomers if they are made up of the same number and types of atoms, but differ in the arrangement of these atoms.

Stereoisomerism in Vinyl Polymers

Polymerization of a vinyl monomer, $\text{CH}_2=\text{CHX}$, where X may be a halogen, alkyl or other chemical group (anything except hydrogen!) leads to polymers with microstructures that are described in terms of *tacticity*.



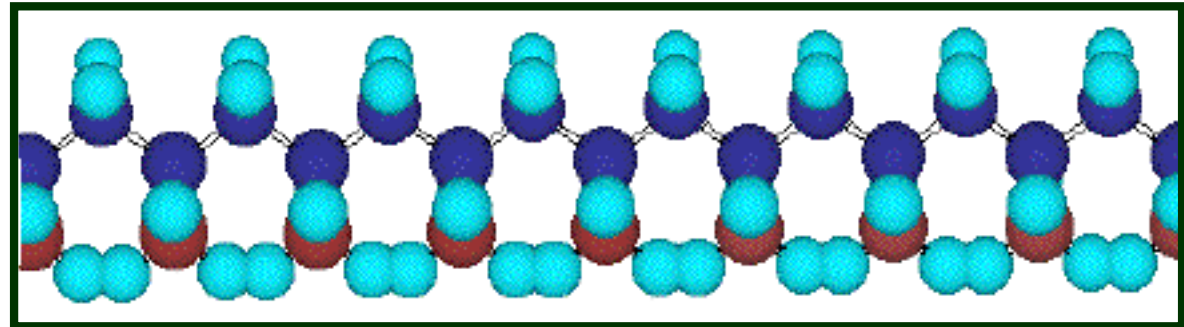
Meso Diad



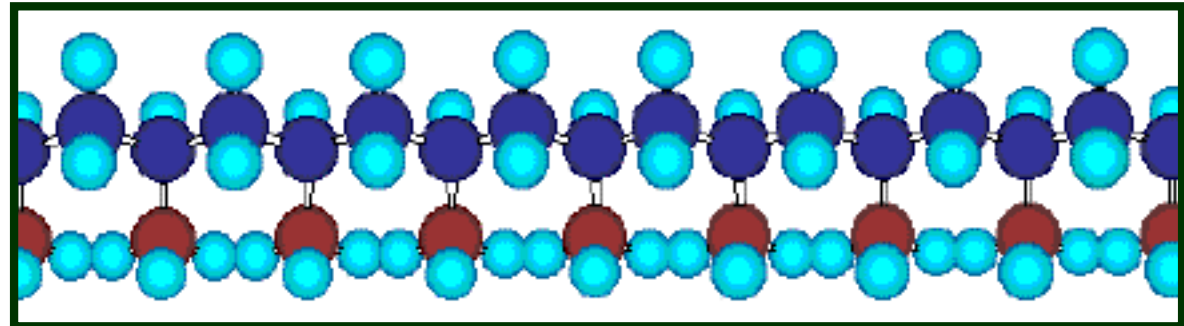
Racemic Diad

Isotactic Chains

Part of an isotactic polypropylene chain seen from the side



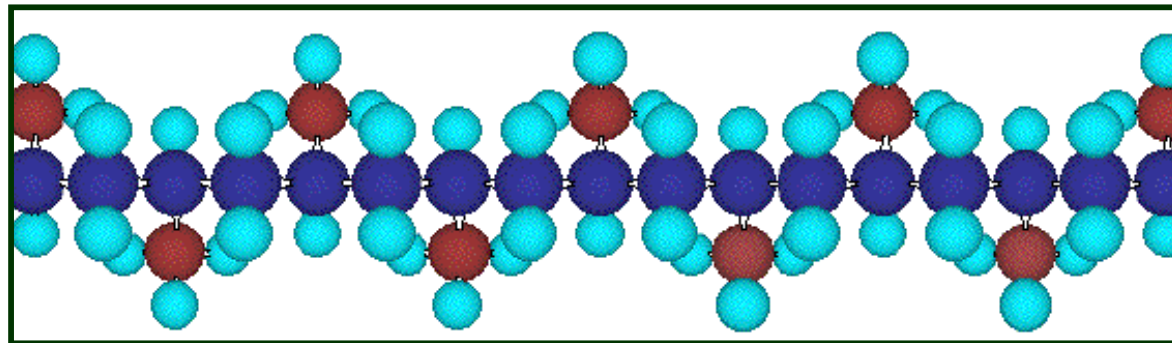
The same chain seen more from the top



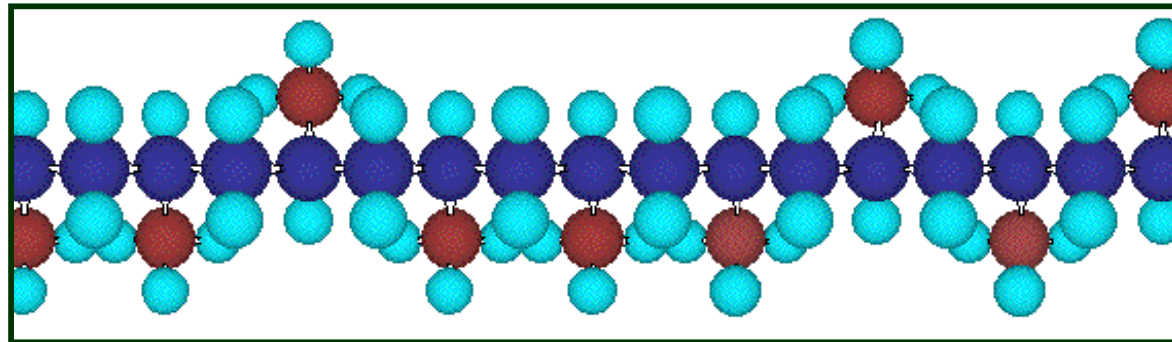
Syndiotactic Chains

Here are two more polypropylene chains, both shown as if we were looking down from "on top". One of these consists of units that are all racemic to one another and is called *syndiotactic*. The other has a random arrangement of units and we call such chains *atactic*. Which one is the atactic chain, A or B?

A



B



Tacticity in Some Commercially Important Polymers

- Polystyrene - atactic
- Polypropylene - largely isotactic
- PVC - largely atactic
(*Some syndiotactic sequences ?*)
- PMMA - atactic