3D Printing: Polymer Chemistry

RPI STEAMM Inventor's Studio Summer Program

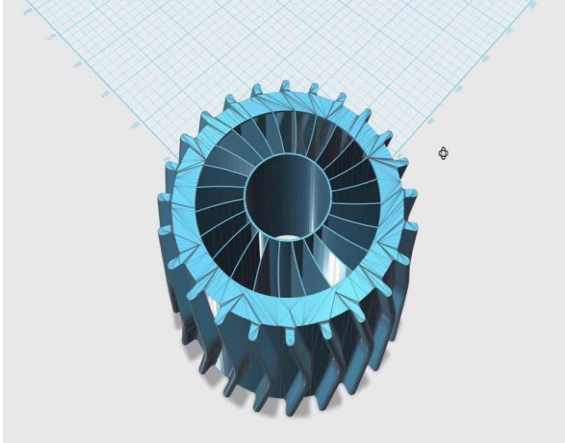
Lauren Zakrzewski

Introductions

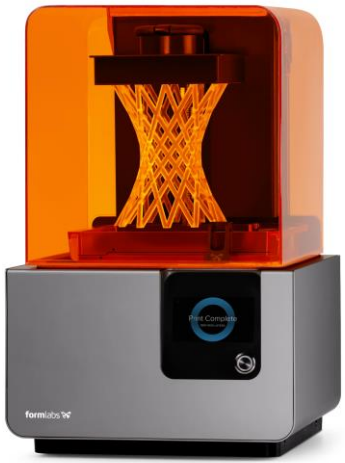
Lauren Zakrzewski

- 5th year Doctoral Student
- Chemistry & Chemical Biology (C&CB) Department
- Research advisor(s):
  - Dr. Chulsung Bae (C&CB department)
  - Dr. Catalin Picu (MANE department)
- Performing research in Polymer Chemistry for the late Dr. Chang Ryu

3D Printing Overview



- Method of manufacturing commonly called Additive Manufacturing (AM)
- Based off of a CAD drawing (Computer-aided design)
- CAD drawing converted to a digital file that can relay instructions to the 3D printer



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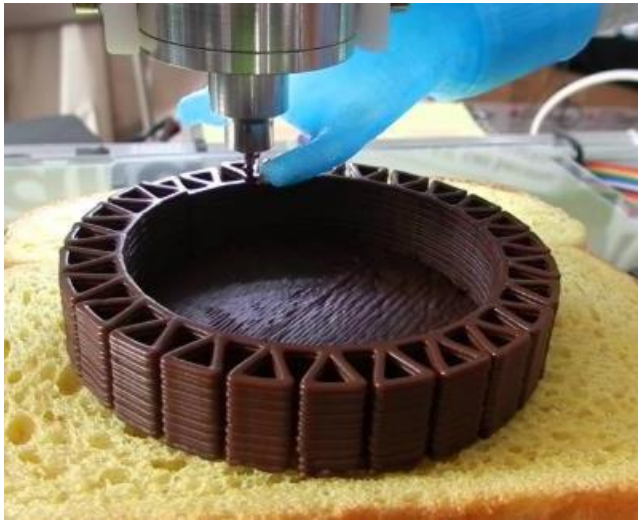
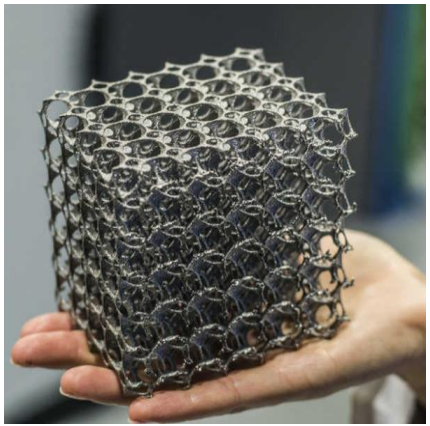
3D Printing Materials

- Plastics/Polymers- acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), photocurable resins (epoxies, acrylics, etc.)
- Metals- stainless steel, titanium, copper, etc.
- Carbon fiber
- Food





3D Printing Materials Before and After

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Polymers in Everyday Life

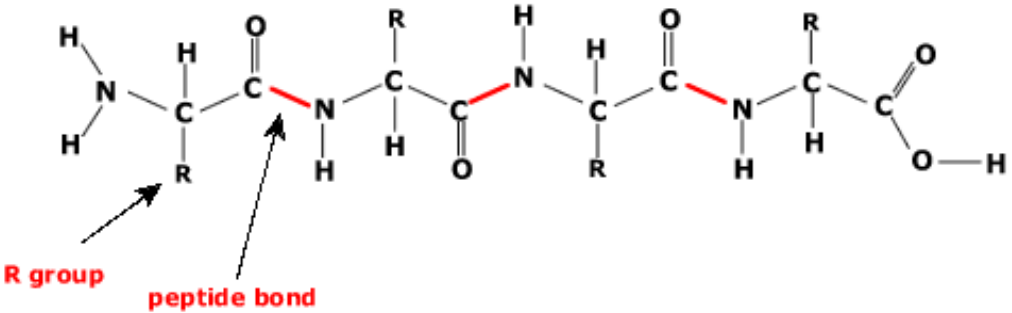
- Polymers can be found everywhere
- They are found in nature or can be manmade
- Natural Polymers can often influence Synthetic Polymers

Natural Polymers

- Occur in nature, and are extracted for everyday use
- They can come from animals, plants, and microorganisms
- They have applications in biomedicine, technology, and everyday items

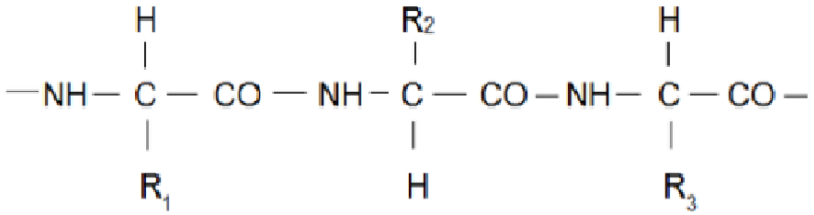
Natural Polymers - Silk

- Silk is a naturally occuring polymer containing sericin and fibroin
- Comes from spiders and other insects
- Silk can be used in cloth, bandaging, gels, tissue engineering



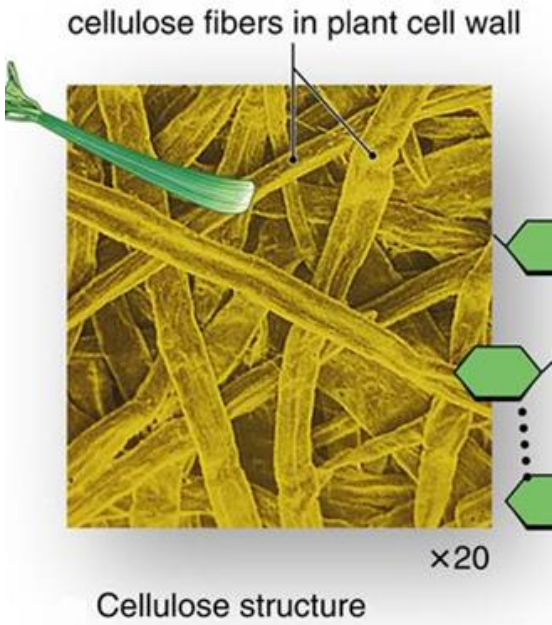
Natural Polymers- Wool

- Wool Fibre contains natural polymers
- Occurs in many mammals
- Contains the protein keratin
- Wool is used in clothing, interior design, blankets, and insulation

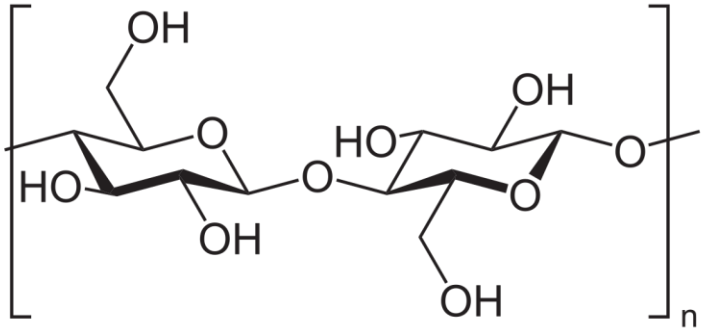


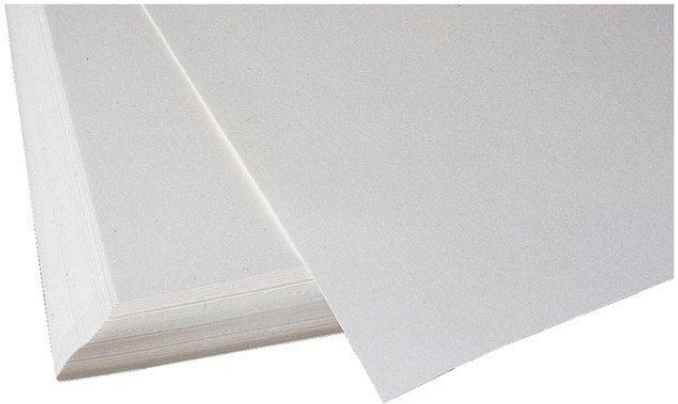
Natural Polymers- Cellulose

- Cellulose is one of the most frequently occurring natural polymers
- Found in the stalks and stems of plants
- Contains glucose molecules
- Can be used to make paper, cardboard, textiles, and renewable fuel



Cellulose structure



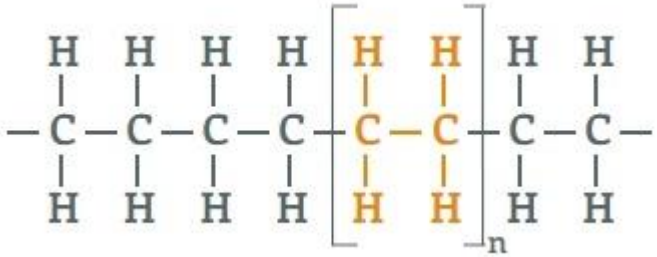


Synthetic Polymers

- Man made polymers for specific uses and containing specific properties
- Often derived from petroleum oils
- They have applications in materials science, technology, and everyday items

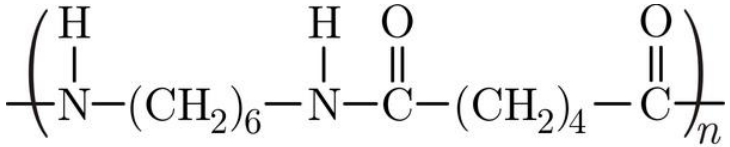
Synthetic Polymers- Polyethylene

- One of the most common plastics used today
- High density or low density can be used to make object with different properties
- Used largely for packaging, which has applications in almost every industry

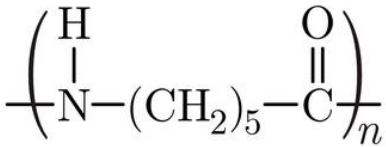


Synthetic Polymers- Nylon

- Nylon can be used in the textile industry, and as a plastic
- Nylon 6 is a type that is used in industrial fabrics and yarns
- Nylon 66 has applications in sportswear, car airbags, parachutes, and tires



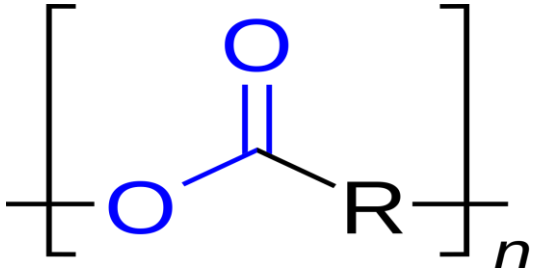
Nylon 66

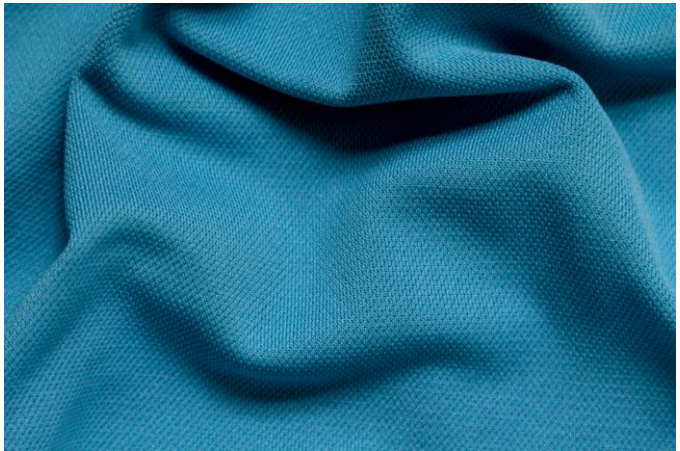


Nylon 6

Synthetic Polymers- Polyester

- Polyester has textile applications, and is one of the worlds most commonly used fabrics
- Sometimes combines with other naturally occurring or synthetic fibers to make cloth blends
- Seen in clothing, blankets, fabrics, and sheets





Review!

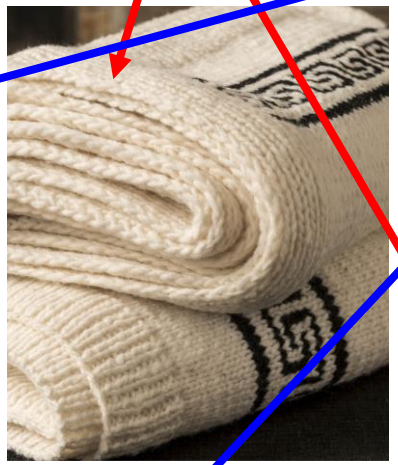
Take 5-10 minutes to identify if the following objects are made up of natural or synthetic polymers

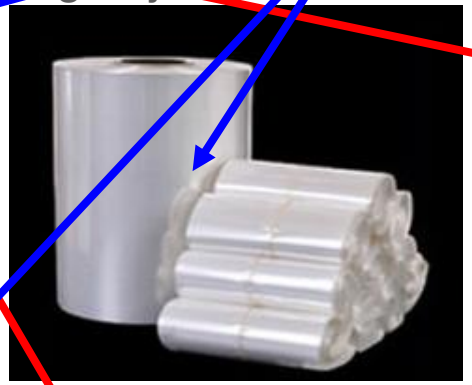
Review!

Natural

Synthetic

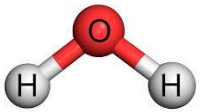
Take 5-10 minutes to identify if the following objects are made up of natural or synthetic polymers



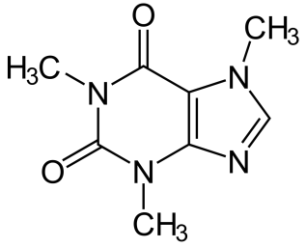


Polymer Chemistry Introduction

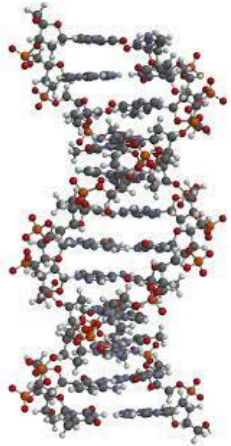
- Molecule:
  - A group of 2 or more atoms connected together by chemical bonds
- Monomers:
  - Molecules that can chemically react with each other
  - Commonly referred to as “Building Blocks”
- Polymers:
  - Large molecules made up of many repeating subunits
- Polymerization:
  - A chemical reaction in which monomers are chemically combined to make long chains of the same subunit (polymers)



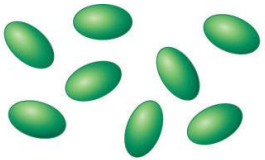
Water



Caffeine



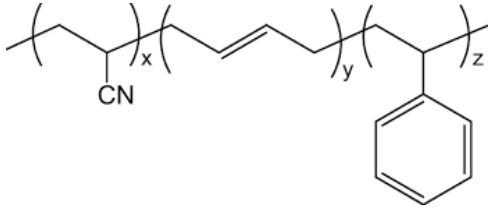
DNA



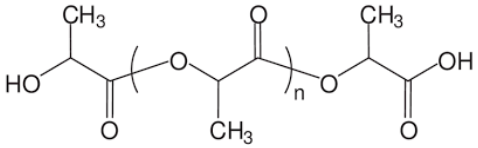
Monomers

Polymer Chemistry

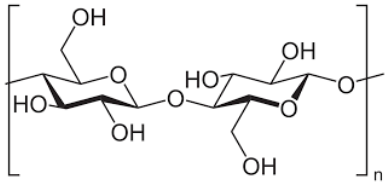
- Examples of polymers:
  - ABS, PLA, cellulose, DNA, etc.
- Polymers can be seen in everyday objects



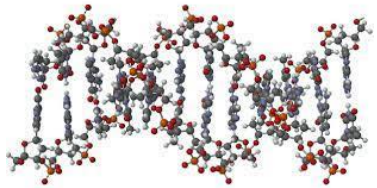
Acrylonitrile butadiene styrene (ABS)



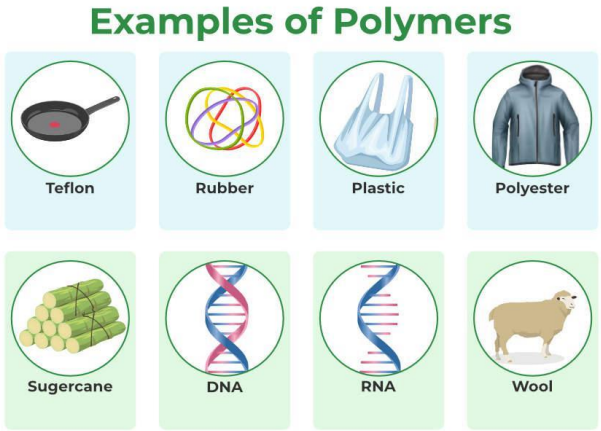
Polylactic acid (PLA)



Cellulose



DNA



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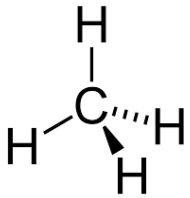
Review!

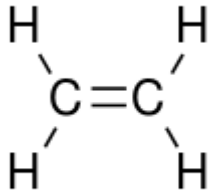
- Take 5 minutes to decide if each chemical structure is a molecule, a polymer or both

1.



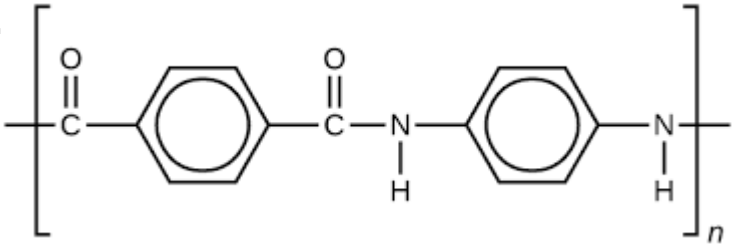
Methane

2.



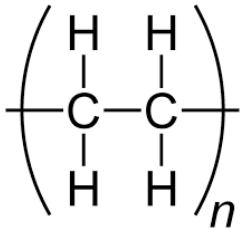
Ethene

3.



Kevlar

4.

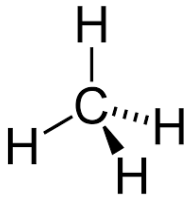


Polyethylene

Review!

- Take 5 minutes to decide if each chemical structure is a molecule, a polymer or both

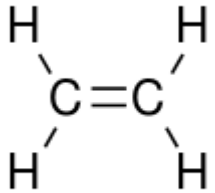
1.



Methane

Molecule

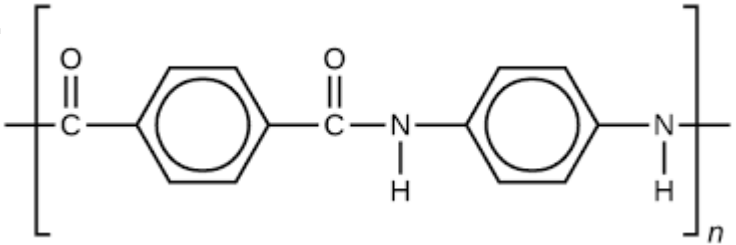
2.



Ethene

Molecule

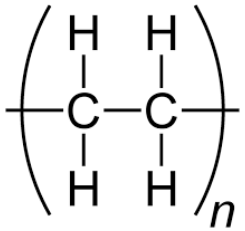
3.



Kevlar

Molecule & Polymer

4.



Polyethylene

Molecule & Polymer

Common Polymers

Polyethylene

Polytetrafluoroethylene
(Teflon)

Polyvinyl chloride
(PVC)

Polynucleotide
(DNA)

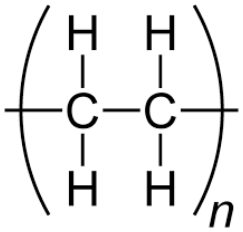
Polyepoxides
(Epoxy Resin)

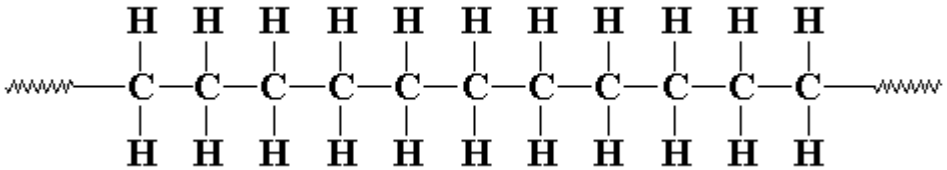
Polyisoprene
(Natural Rubber)

Polymer Notation

This group repeats along the chain **n** times

Poly(ethylene)

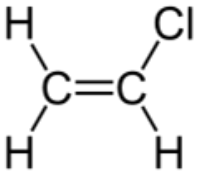


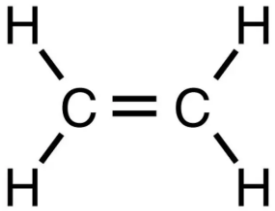


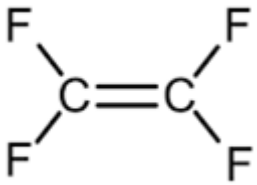
Review!

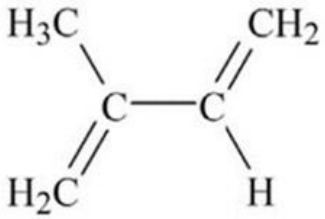
- Take 5 minutes to match each monomer to its polymer

Monomers

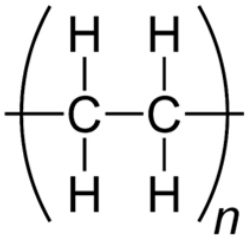




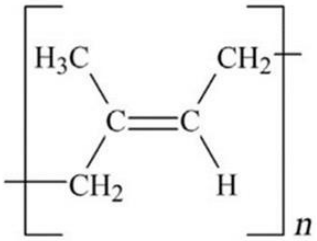




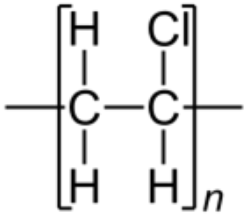
Polymers



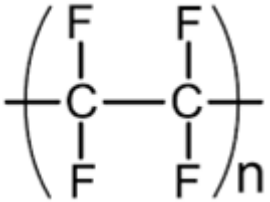
Polyethylene



Polyisoprene



Polyvinyl chloride

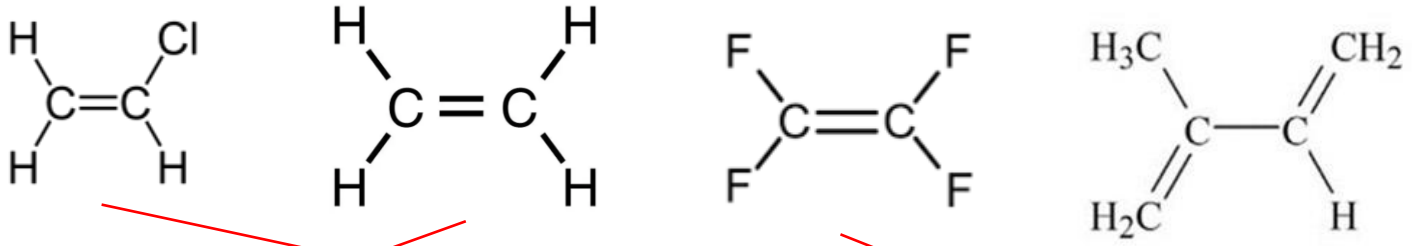


Polytetrafluoroethylene

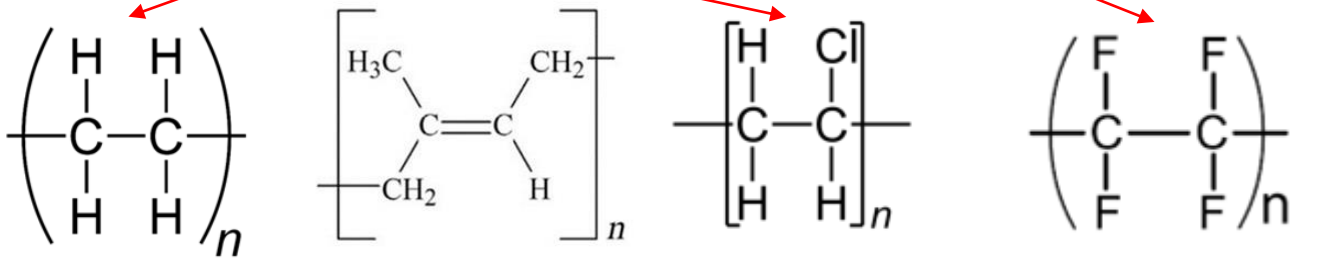
Review!

- Take 5 minutes to match each monomer to its polymer

Monomers



Polymers



Polyethylene

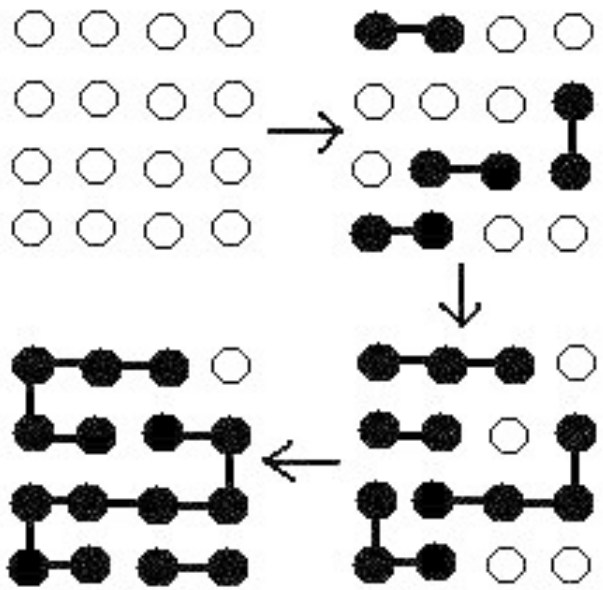
Polyisoprene

Polyvinyl chloride

Polytetrafluoroethylene

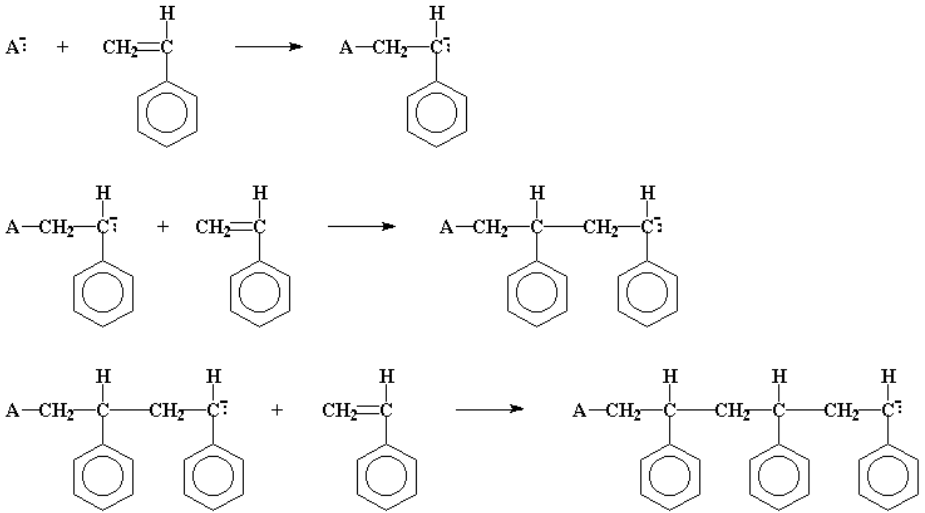
Polymers -Step Growth

- Also referred to as condensation polymerization
- Reactions occur between functional groups of different molecules
- Reactions occur rapidly



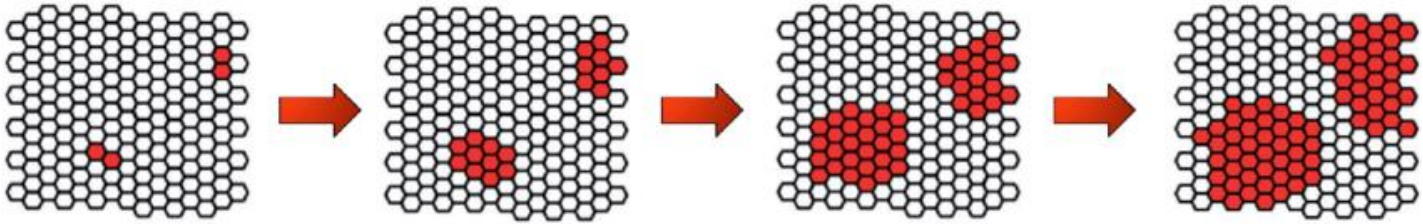
Polymers- Chain Growth

- Also referred to as addition polymerization
- Reactions occur as more polymer subunits are added to the end of a chain
- Forms from unsaturated monomers
    - Unsaturated contains carbon-carbon double bonds

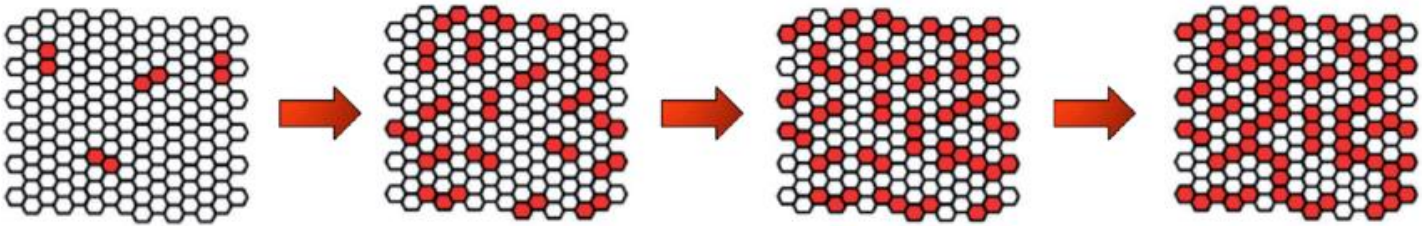


Step Growth vs. Chain Growth

a) chain growth



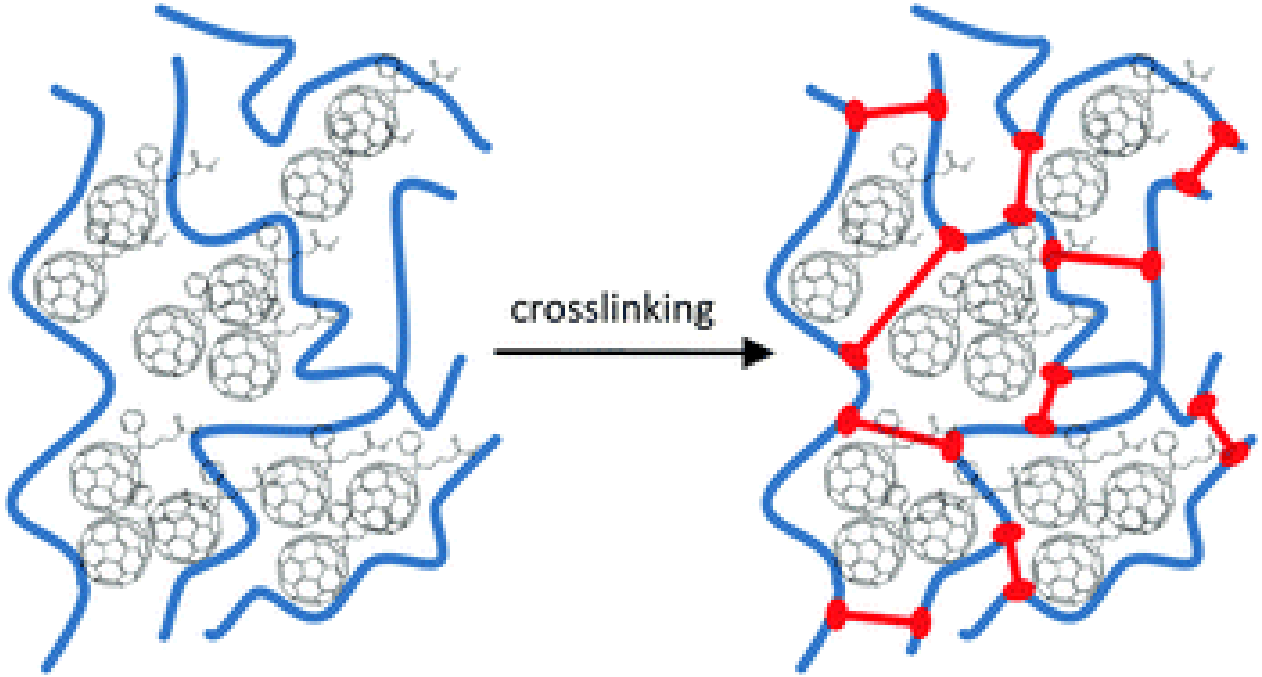
b) step growth



Polymerization

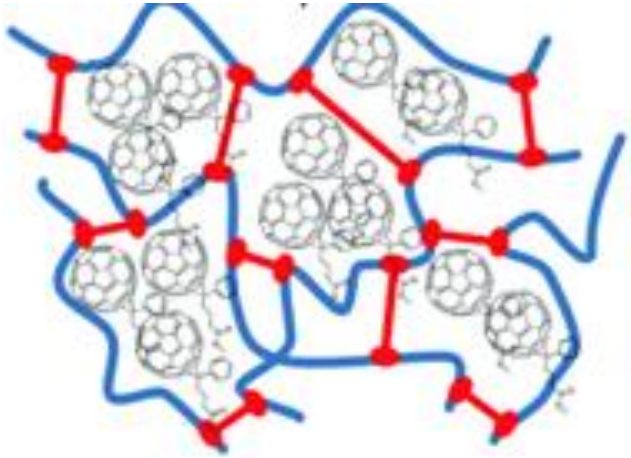
Crosslinking

- When polymer chains are joined together by covalent bonds



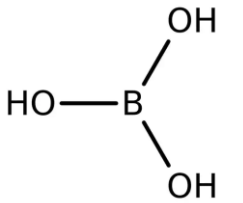
Polymer Putty/Slime Synthesis

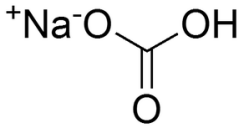
Polymer Putty Synthesis



- Glue [polyvinyl acetate (PVA)]
- Baking Soda [sodium bicarbonate ($NaHCO_3$)]
- Contact Lens Solution
  - Contains Boric Acid [hydrogen borate (H_3BO_3)]

Boric acid combines with baking soda → This combination activates crosslinking between the PVA chains in the glue → The crosslinker makes the glue molecules stick together





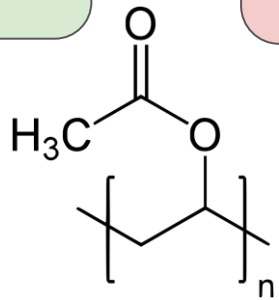
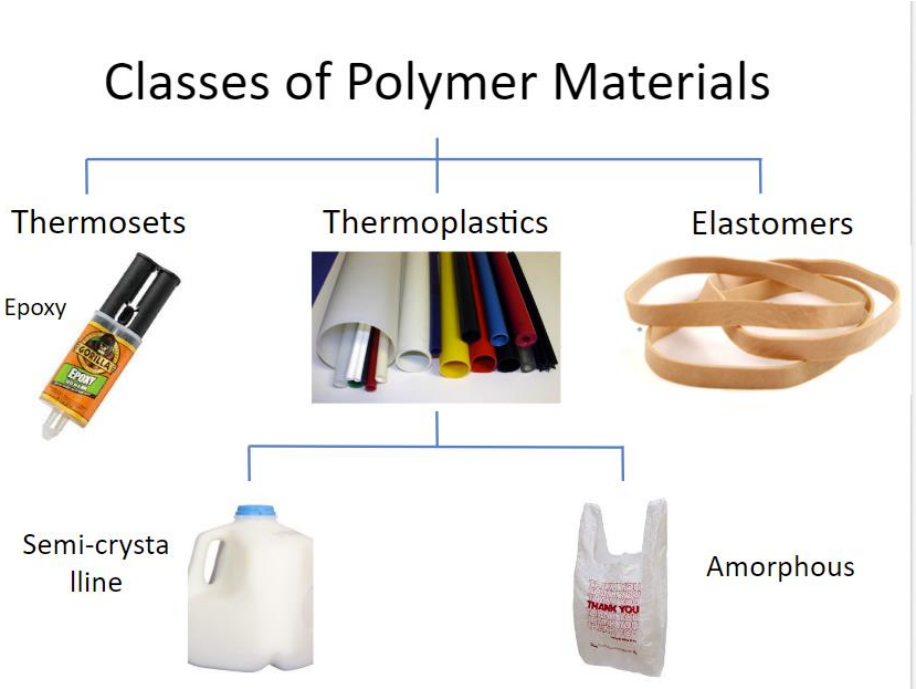
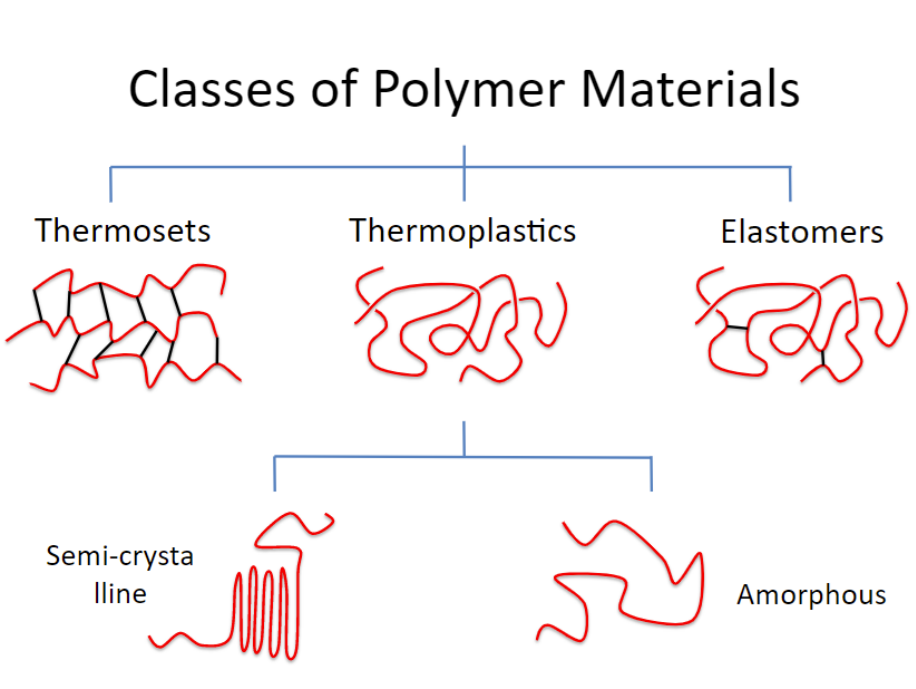


Image Credit to Professor Ed Palermo





- **Thermoset:** Insoluble, hard material, cannot be melted
- **Thermoplastic:** Can be soluble, malleable, can melt
- **Elastomer:** Flexible, lightly crosslinked, can melt

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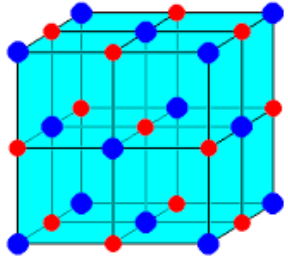
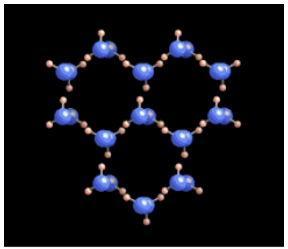
Crystalline Materials (Non-Polymer)

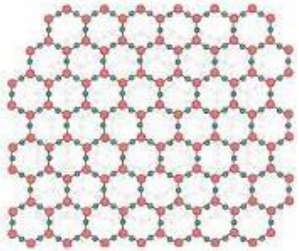
- Molecules are all uniformly packed
- Materials are very hard
- High density



NaCl

Table Salt (NaCl)





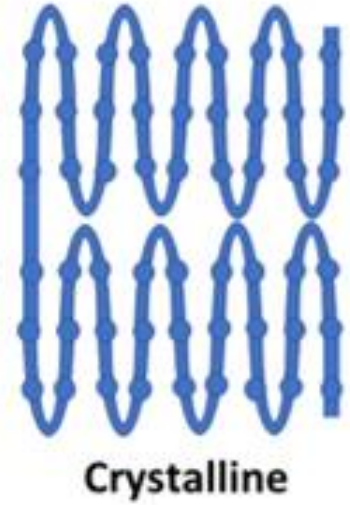
Snowflake (H_2O)

Quartz (SiO_2)

Diamond (C)

“Crystalline” Polymers

- Molecules are all uniformly packed
- Materials are harder
- Opaque (cloudy)
- Higher density
- Polymers will never be 100% crystalline due to the length of their chains
    - Therefore, highly crystalline polymers are referred to as ***semi-crystalline***



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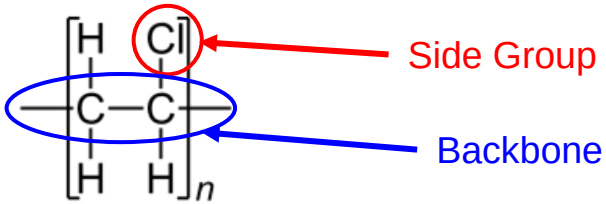
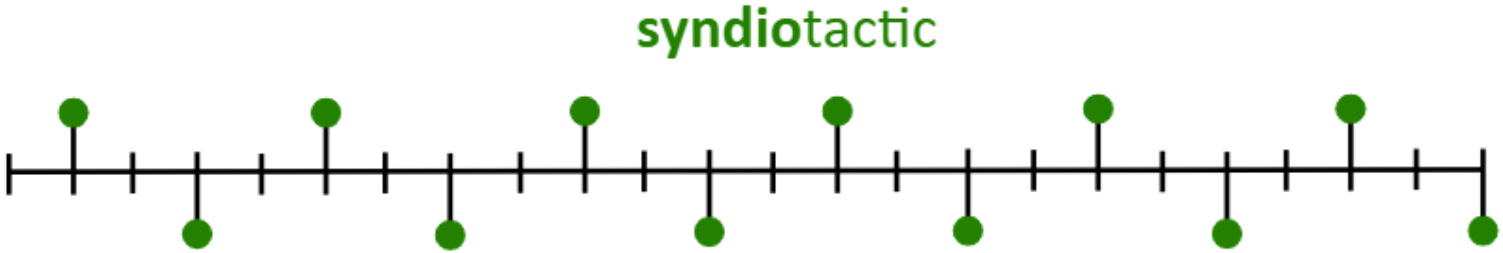
Tacticity



Polyvinyl chloride

Image Credit to Professor Ed Palermo

- Tacticity is the orientation of the side groups attached to the backbone
- Isotactic and syndiotactic are less random, and have a higher crystallinity
- Structures are never 100% isotactic or syndiotactic



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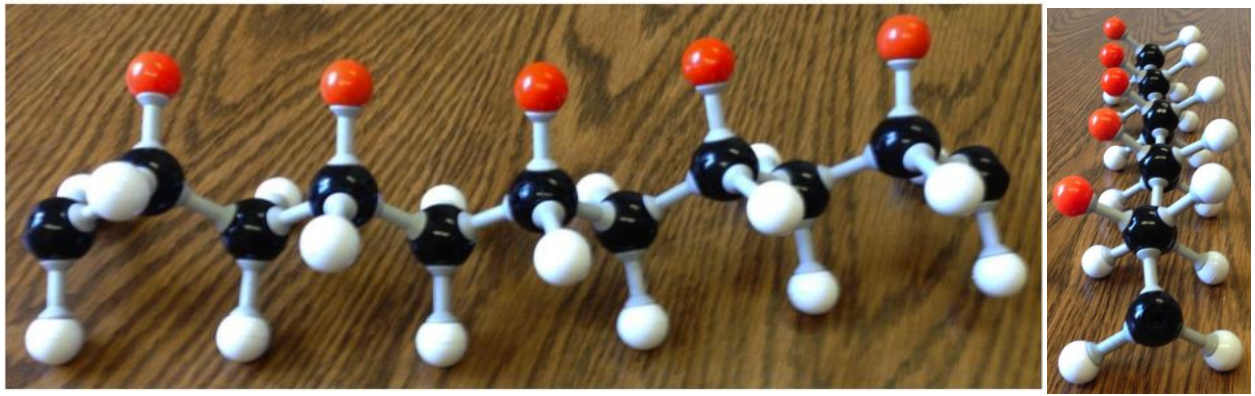
3D Tacticity

Image Credit to Professor Ed Palermo

isotactic



syndiotactic

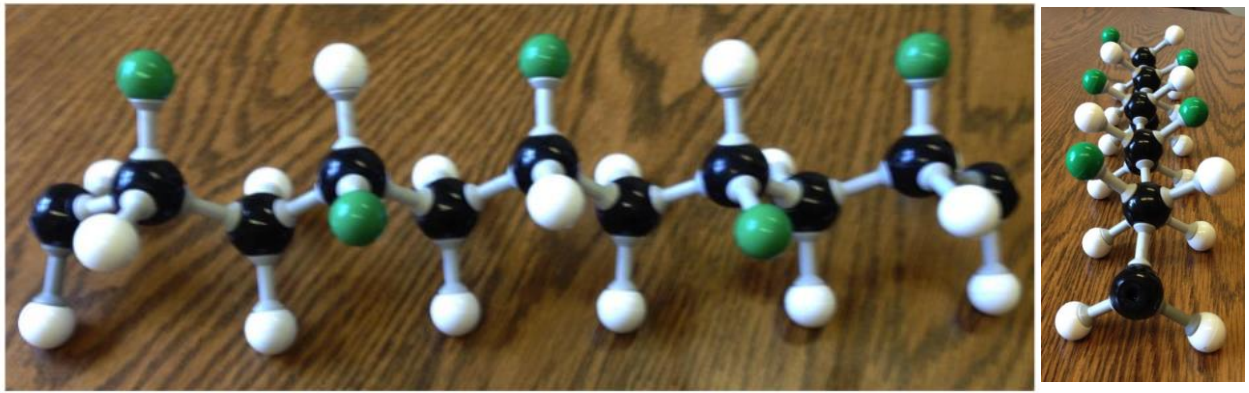
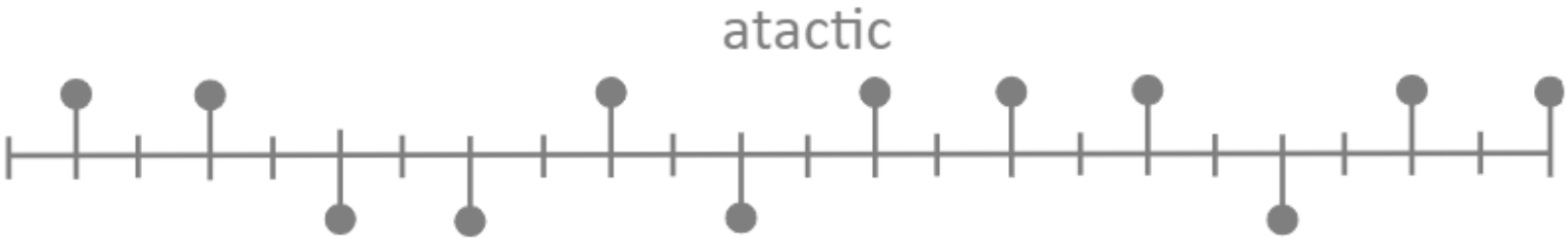


Image Credit to Professor Ed Palermo

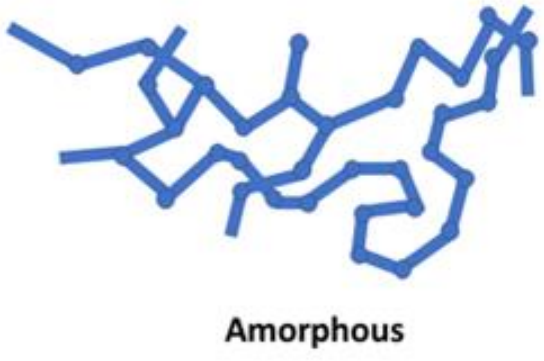
Tacticity

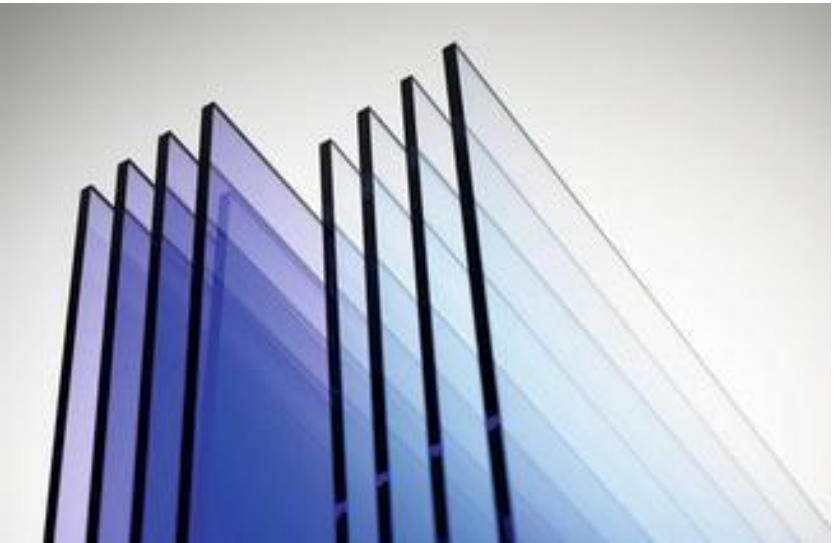
- Atactic refers to a randomized tacticity
- Atactic corresponds with amorphous polymers, due to the lack of order



Amorphous

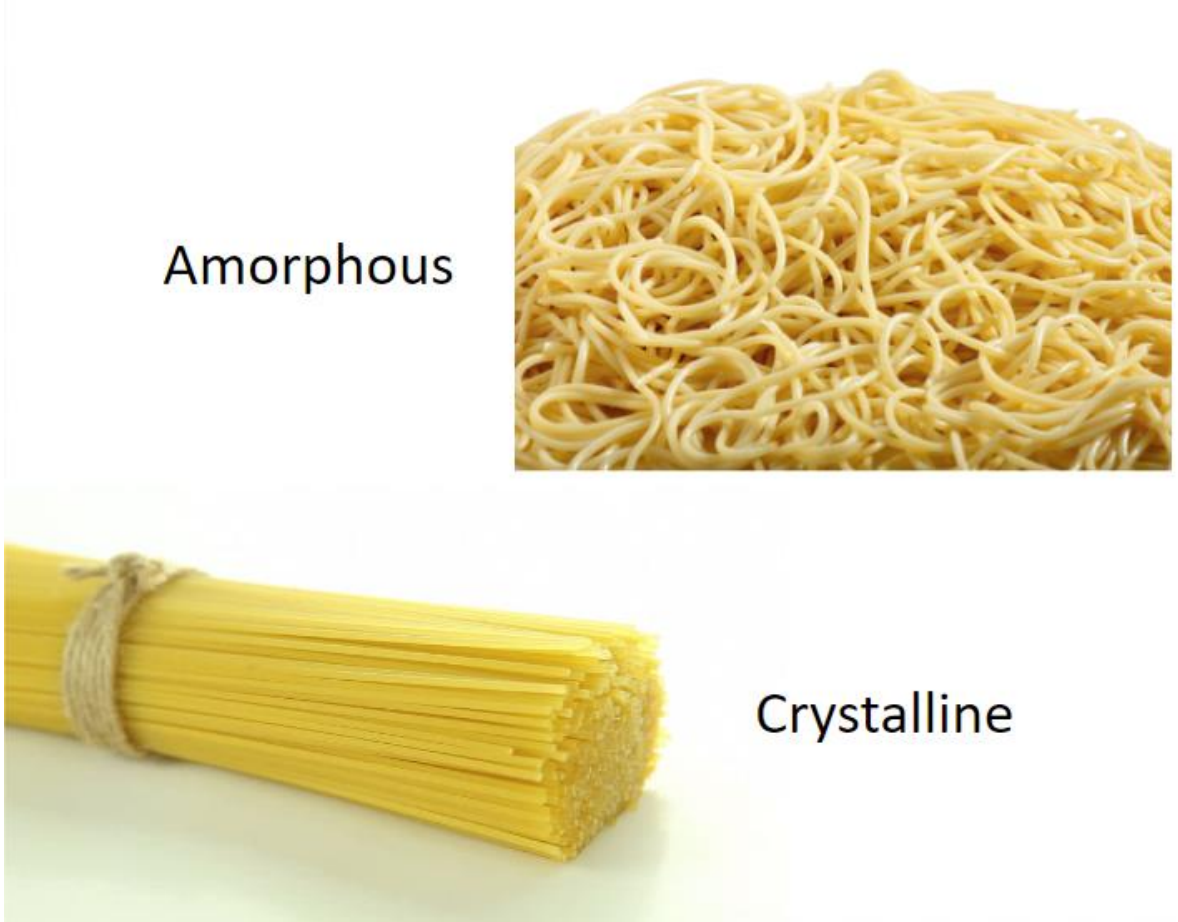
- Molecules are not uniformly packed
- Materials are softer
- Transparent
- Lower Density





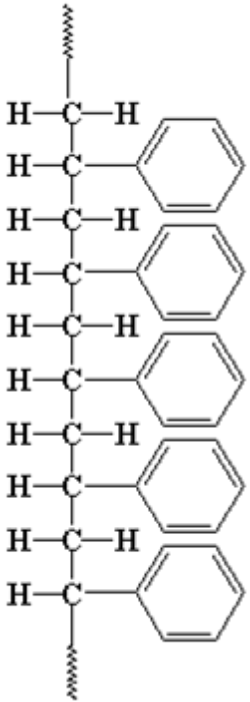
Crystalline vs Amorphous

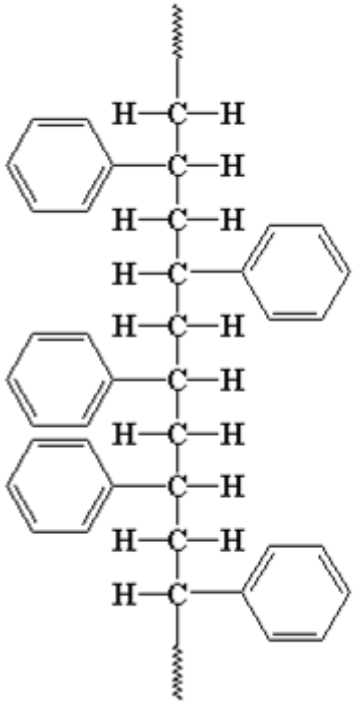
Image Credit to Professor Ed Palermo

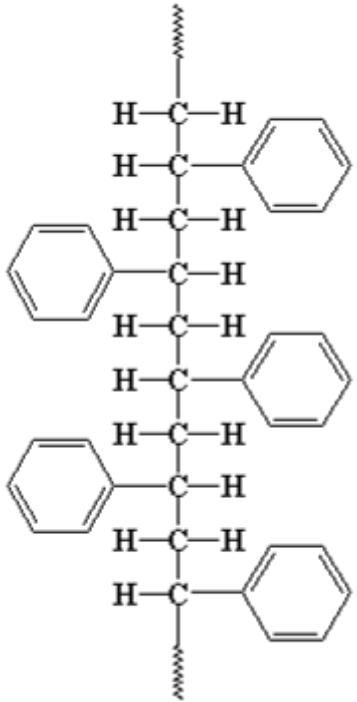


Review!

- Take 5 to 10 minutes to identify the tacticity of each polymer chain







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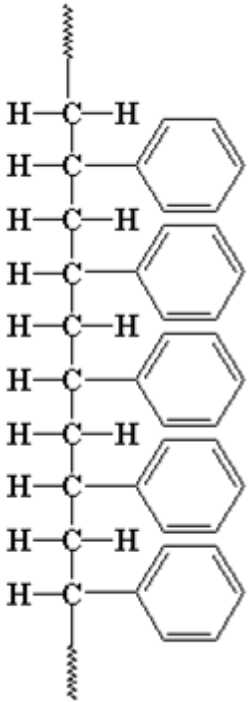
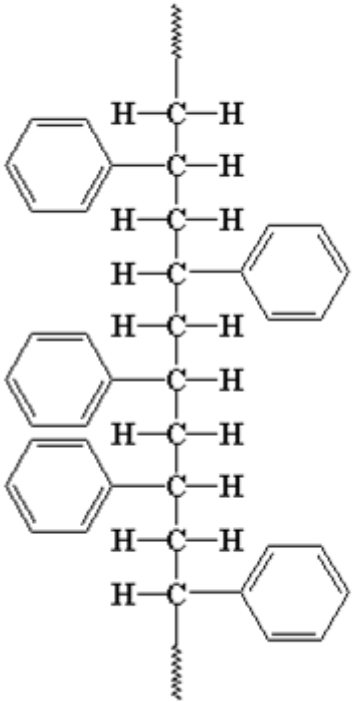
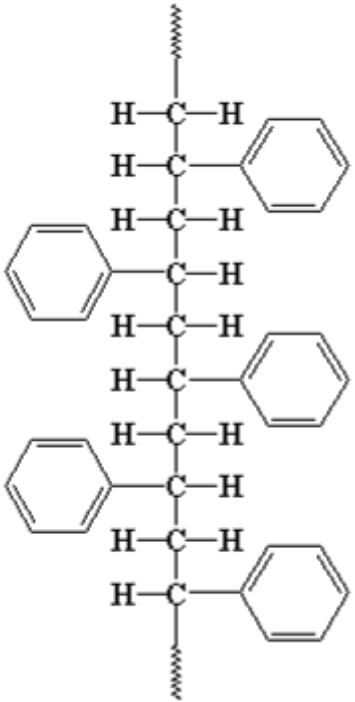


Isotactic



Atactic

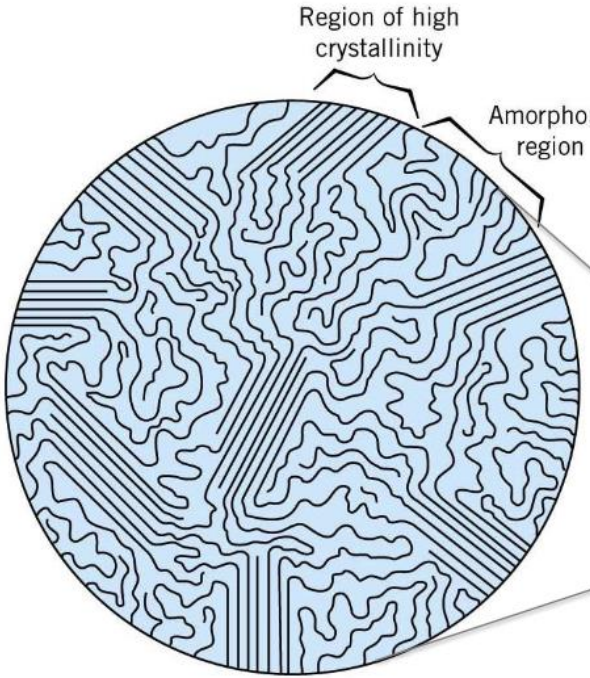


Syndiotactic

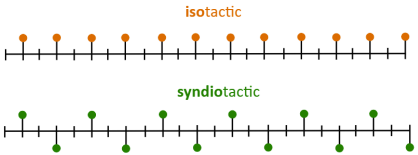
Semi-Crystalline

Image Credit to Professor Ed Palermo

High Density Polyethylene: Milk Cartons

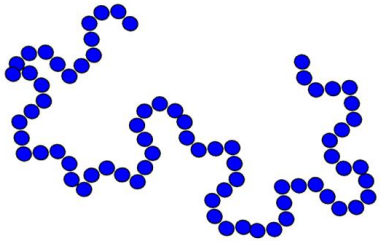


- Contains parts that are crystalline AND amorphous
- More flexible than crystalline, but not as flexible as amorphous

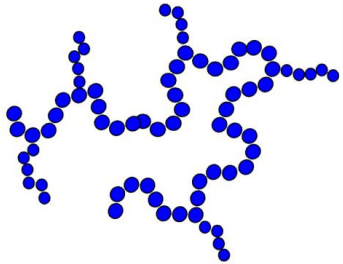


Polyethylene

Low Density

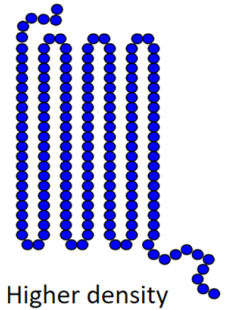


Lower density

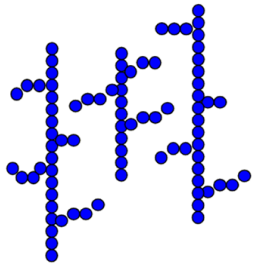


Lower density

High Density

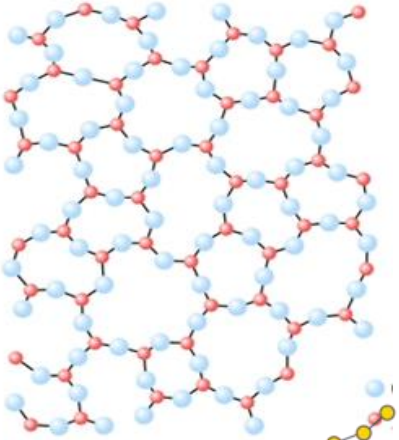


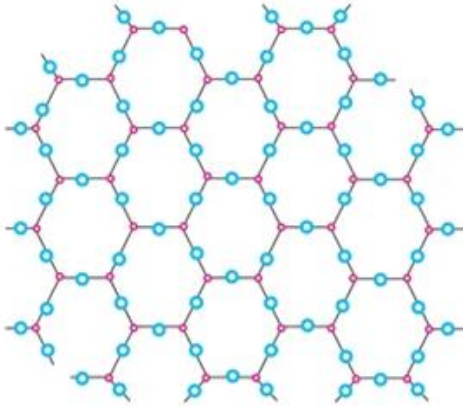
Higher density

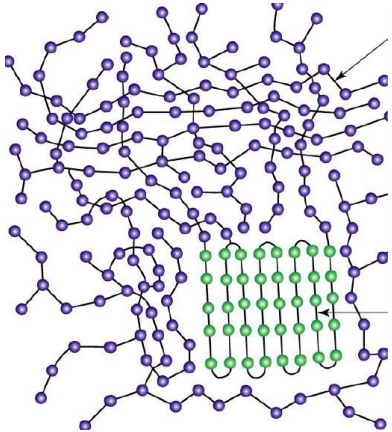


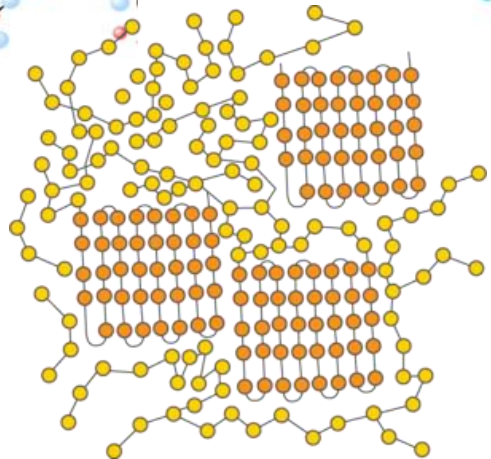
Review!

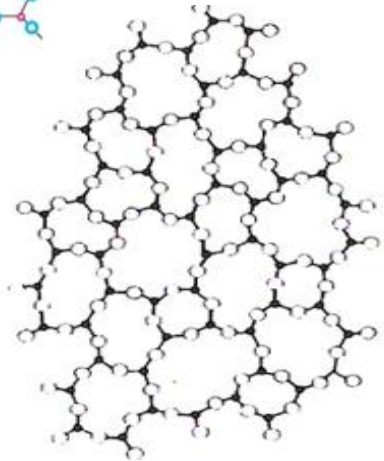
- Take 5-10 minutes to identify the crystallinity of each microstructure











Review!

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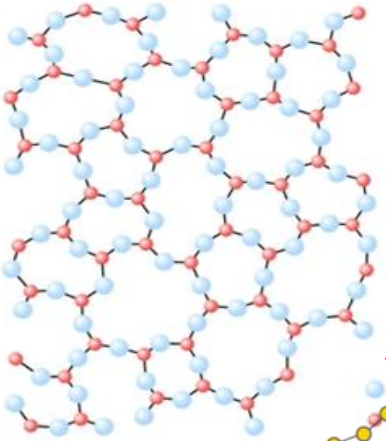
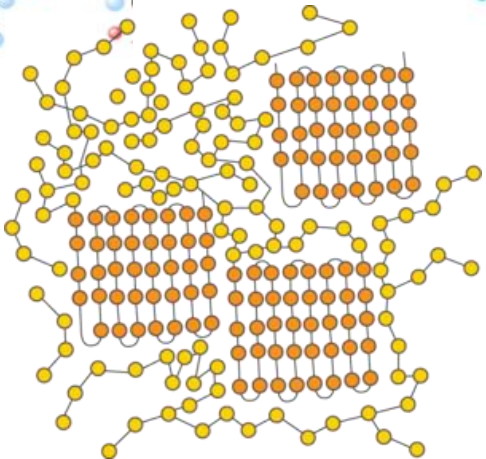
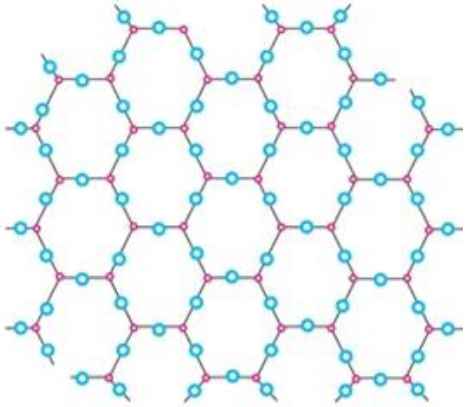


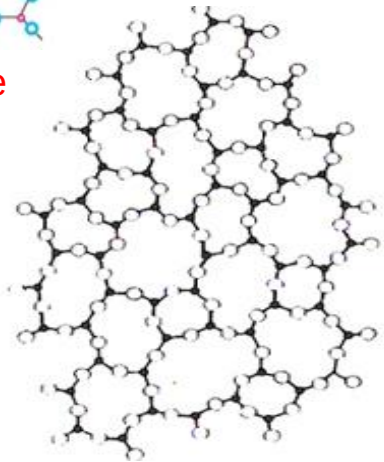
Amorphous



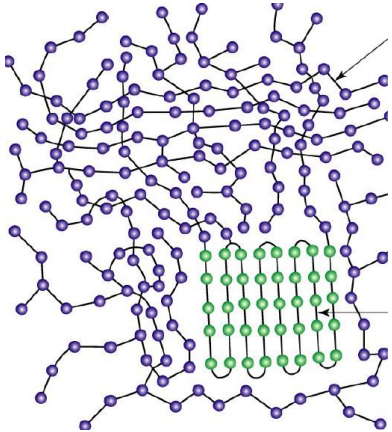
Semi-Crystalline



Highly Crystalline



Amorphous



Semi-Crystalline

Questions?