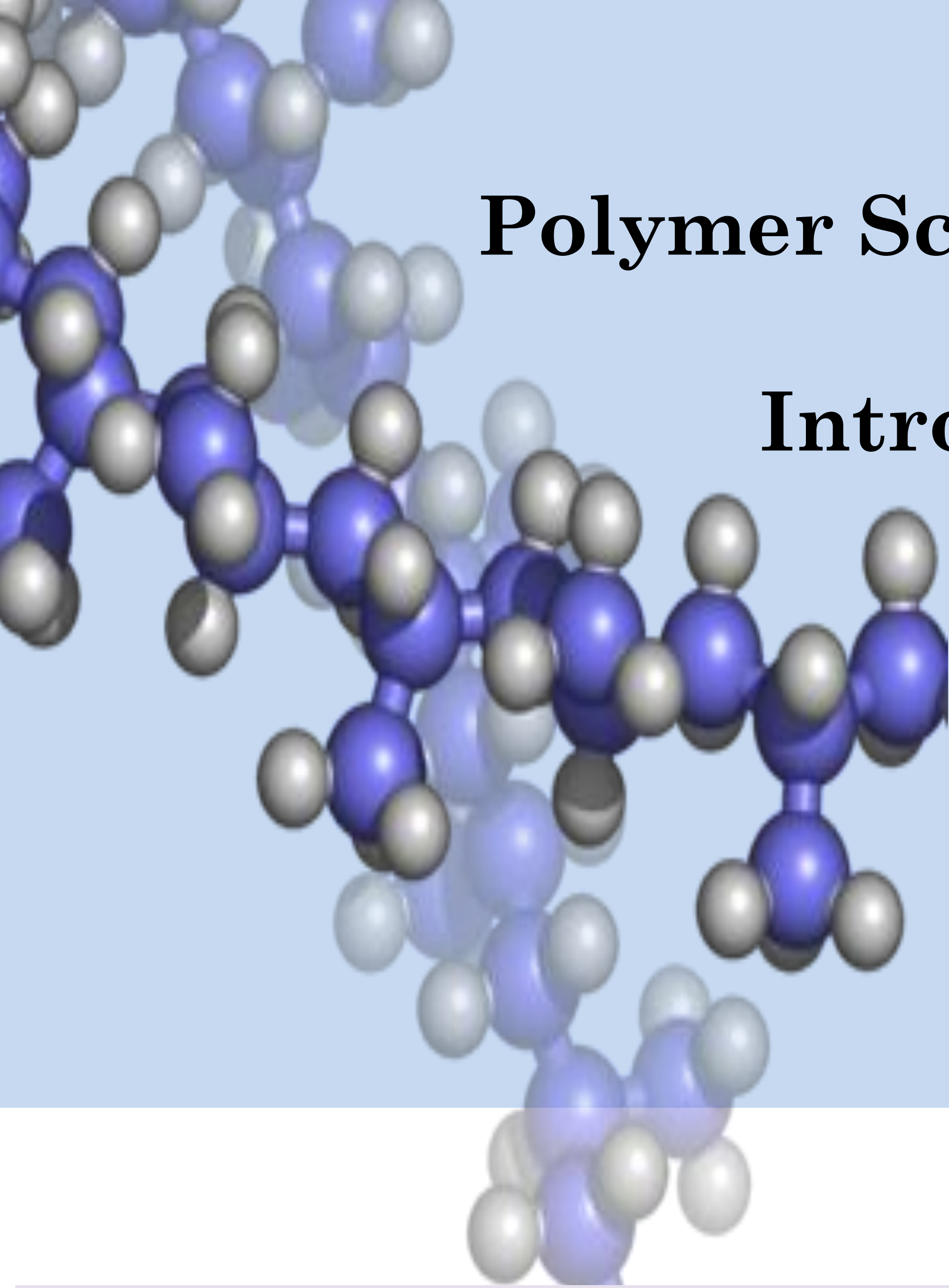


# Polymer Science & Engineering

## Introduction: Definitions

Dr. Motasem Saidan

m.saidan@gmail.com

# Introduction: Definitions

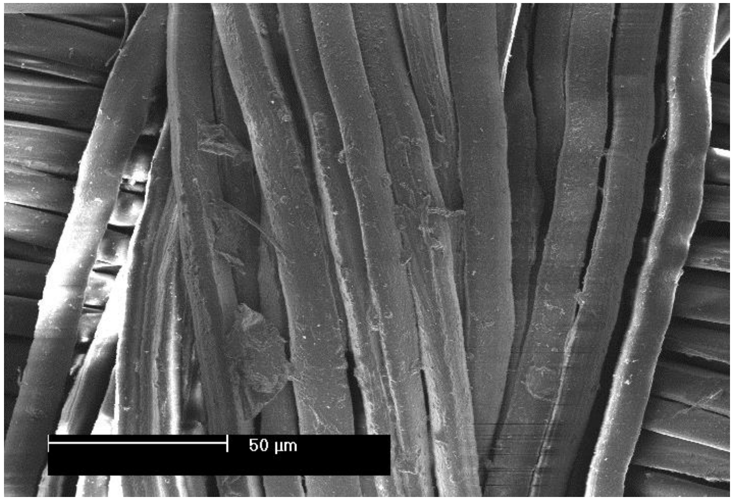
- Greek word "***polumeres***" means `having many parts'

- **Polymer:** large molecule consisting of repeated chemical units (`mers') joined like beads on a string. Polymers usually contain many more than five monomers; some contain hundreds or thousands of monomers in each chain.

- Polymers are natural, such as cellulose or DNA, or synthetic, such as nylon or polyethylene.

- Silk fibre produced by silk worms in a cocoon to protect it while it metamorphoses into a moth.

- Living organisms are mainly composed of polymerized amino acids (proteins) nucleic acids (RNA and DNA), and other biopolymers.

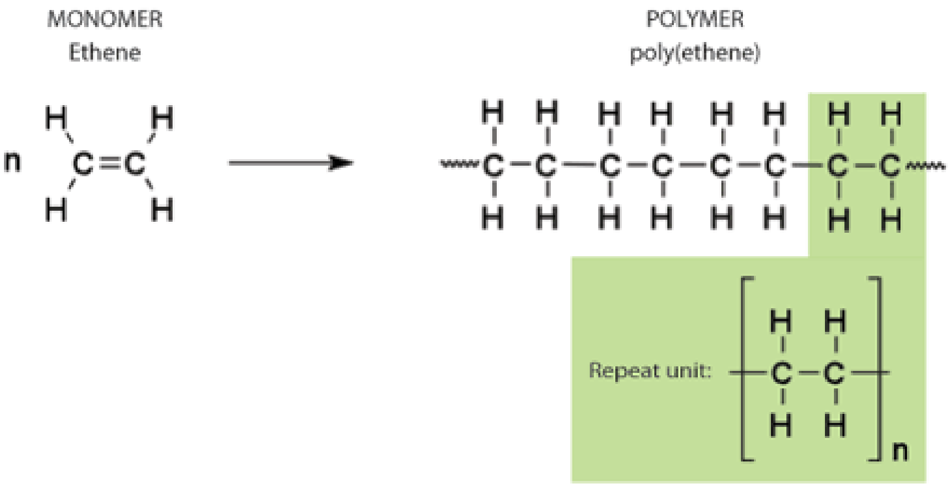


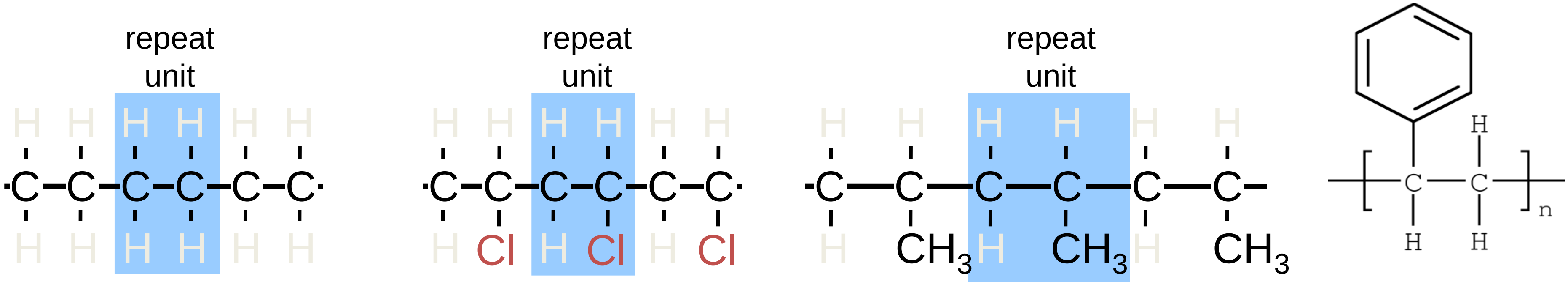

- Our brains are mostly a complex polymer material soaking in salty water!

# What is a polymer?

**Poly** …. **mer**

**many** ………. **repeat unit**



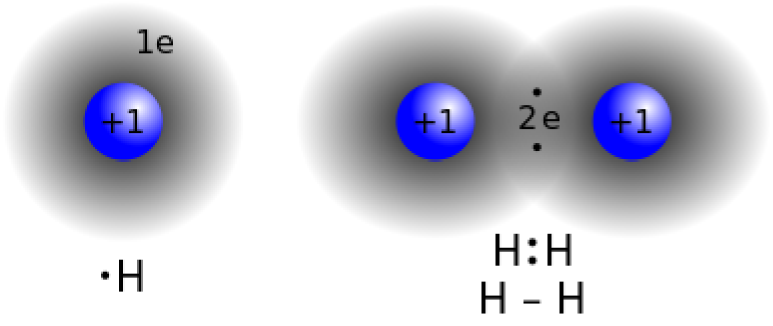



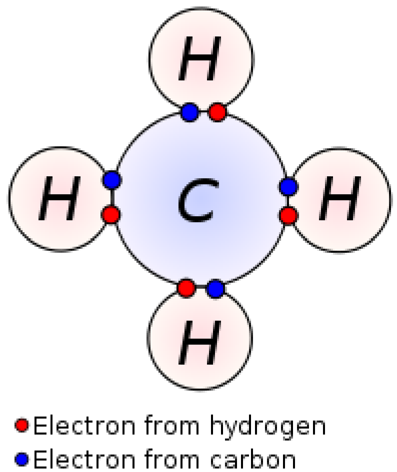

Polyethylene (PE) Polyvinyl chloride (PVC) Polypropylene (PP) Polystyrene (PS)

Adapted from Fig. 14.2, *Callister 7e.*

# Covalent Bond

- Polymers are composed of very large molecules which consist of smaller units, that are tightly bonded together with (strong) **covalent bonds**
- A **covalent bond** is a chemical bond that involves the sharing of electron pairs between atoms. The stable balance of attractive and repulsive forces between atoms when they share electrons is known as covalent bonding.



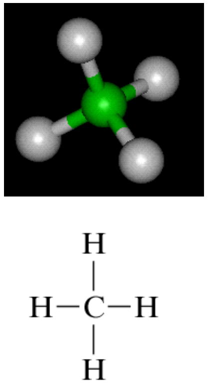



- Polymers are made up of chain molecules ⟶ Long range connections throughout the material.

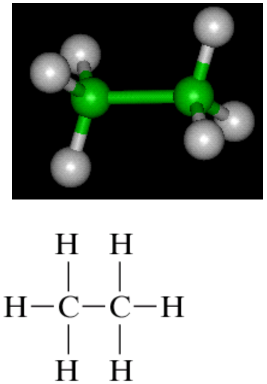
- Polymers are comprised of more than 1000 monomer repeat unit

- Molecular weight ranging between $10^4$ to $10^7$ g/mol

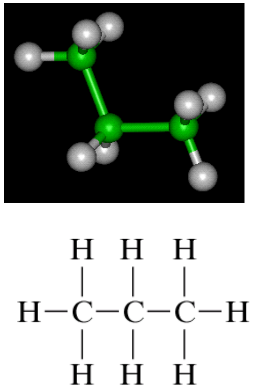
- Most polymers are organic, and formed from hydrocarbon molecules
- Each **C** atom has four ***e-*** that participate in bonds, each ***H*** atom has one bonding ***e-***



**Methane, $CH_4$**

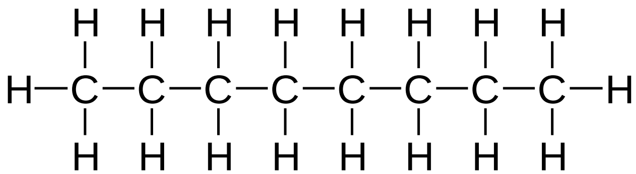


**Ethane, $C_2H_6$**



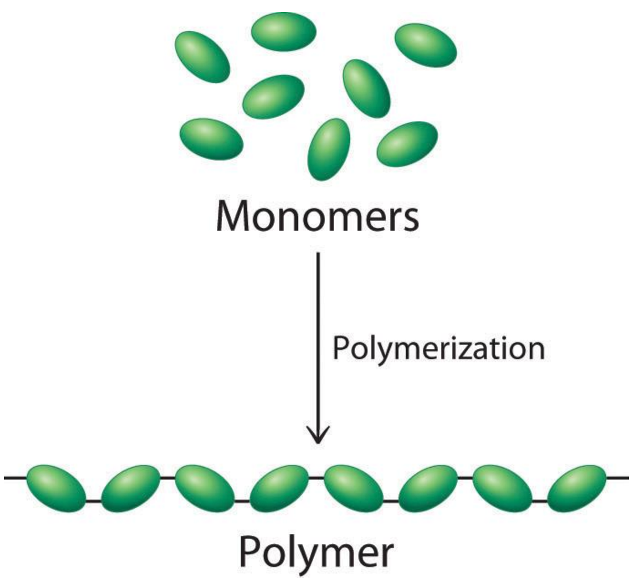
**Propane, $C_3H_8$**

# Polymer Molecule



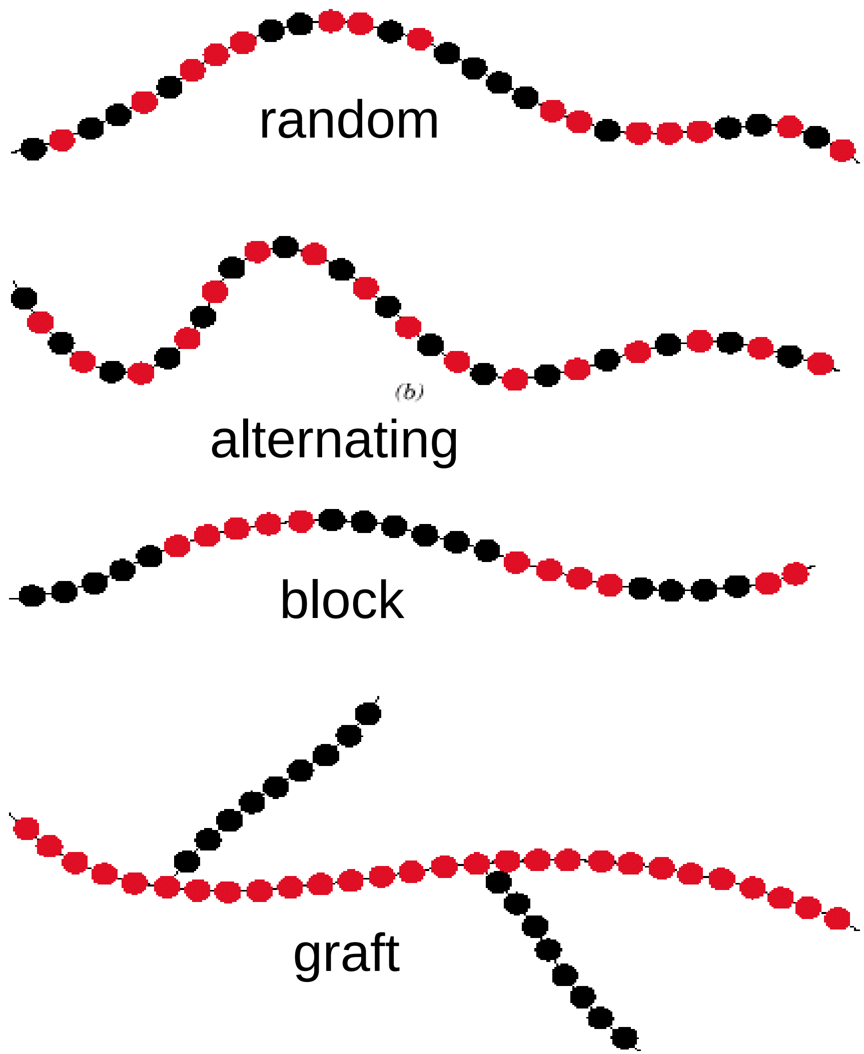
$= H_3C{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$

- Polymer molecules are very large: macromolecules
- Polymers are long and flexible chains with a string of C atoms as a backbone.
- Side-bonding: C to an H or a radical
- Double bonds possible in both chain and side bonds
- Repeat unit (“unit cell”) is a mer
- A single mer is called a monomer
- Homopolymers consist of monomers of the same type;
- Copolymers have different repeating units.



- **Two or more monomers polymerized together**

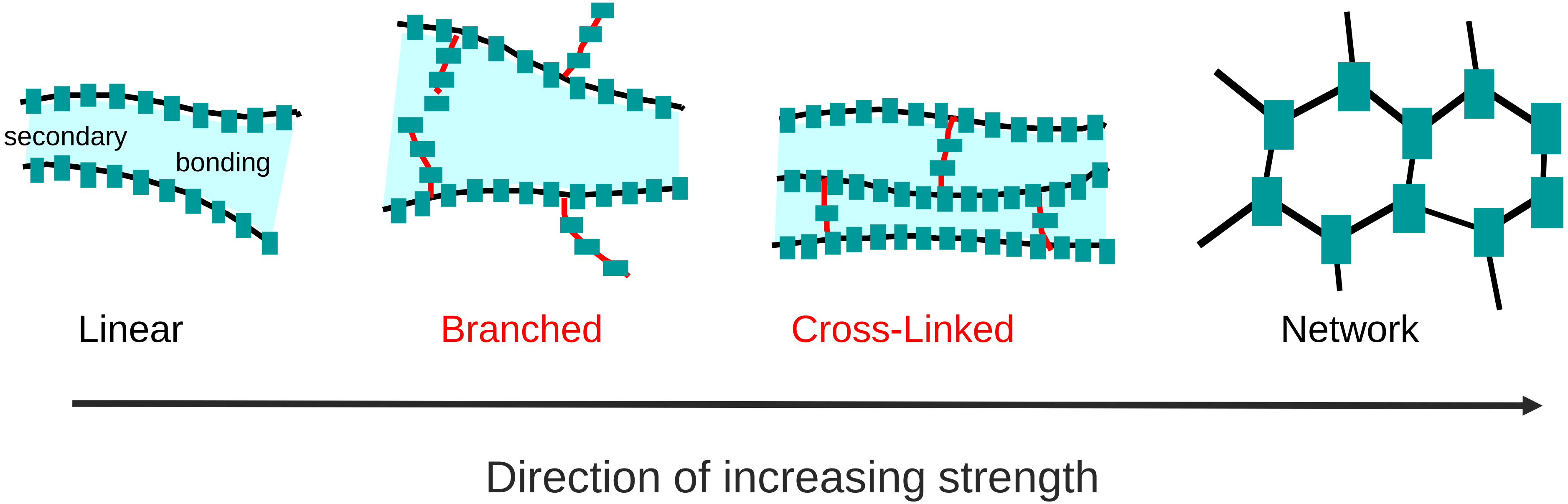
- random – A and B randomly vary in chain
- alternating – A and B alternate in polymer chain
- block – large blocks of A alternate with large blocks of B
- graft – chains of B grafted on to A backbone




**A –** 

**B –** 

# Polymers: Molecular Structures



# Polymer shape: Configuration & Conformation

- The terms **configuration** and **conformation** are used to describe the geometric structure of a polymer and are often confused.

- *Configuration* refers to the order that is determined by chemical bonds. The configuration of a polymer cannot be altered unless chemical bonds are broken and reformed.

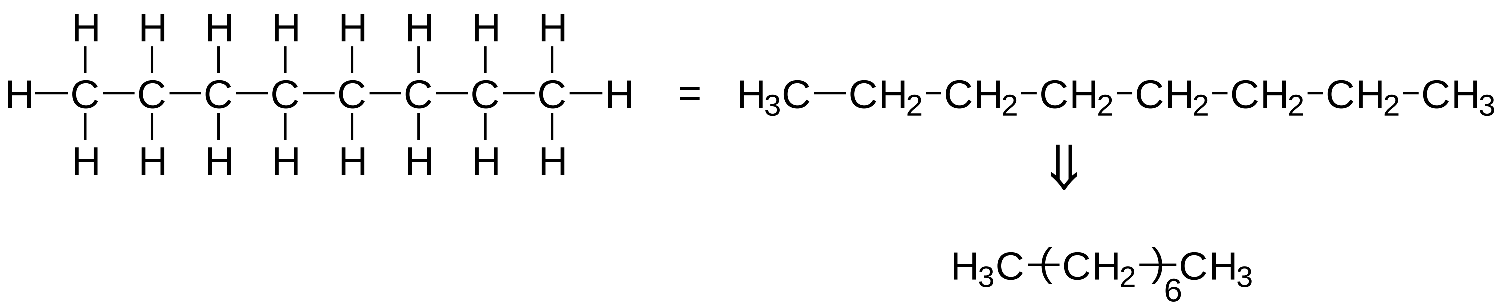
- *Conformation* refers to order that arises from the rotation of molecules about the single bonds.

## Isomerism

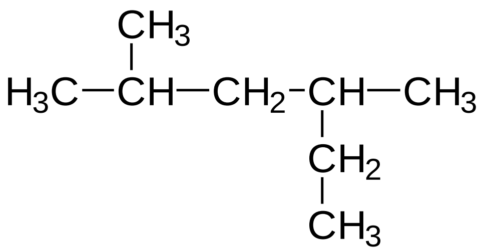
two compounds with same chemical formula can have quite different structures

Ex: $C_8H_{18}$

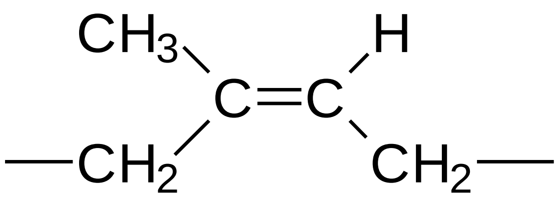
- ✓ n-octane



- ✓ 2-methyl-4-ethyl pentane (isooctane)

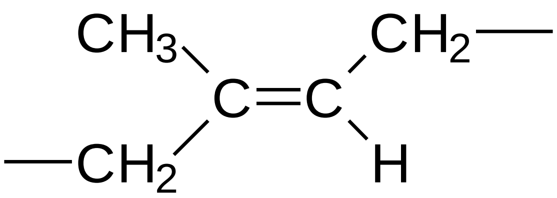


# cis/trans Isomerism




cis

cis-isoprene
bulky groups on same side of chain



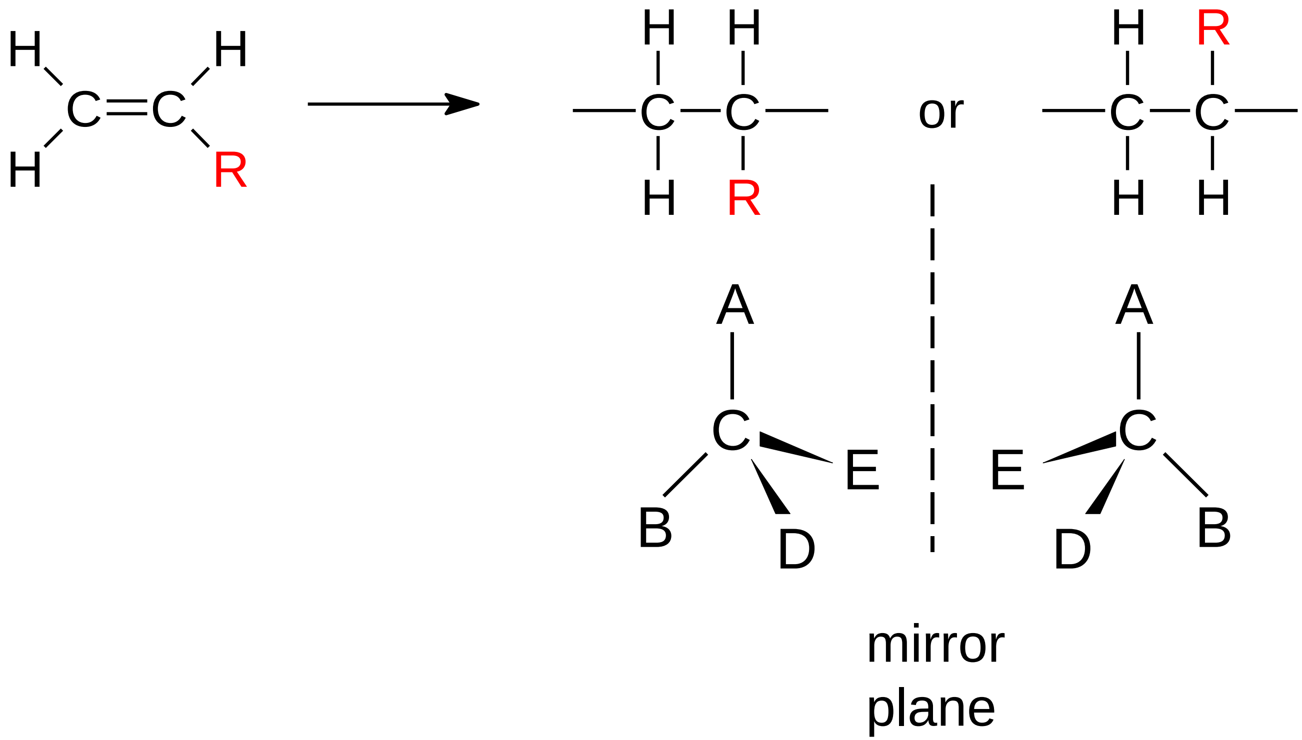

trans

trans-isoprene
bulky groups on opposite sides of chain

# Polymers: Molecular Shape

Configurations – to change must break bonds

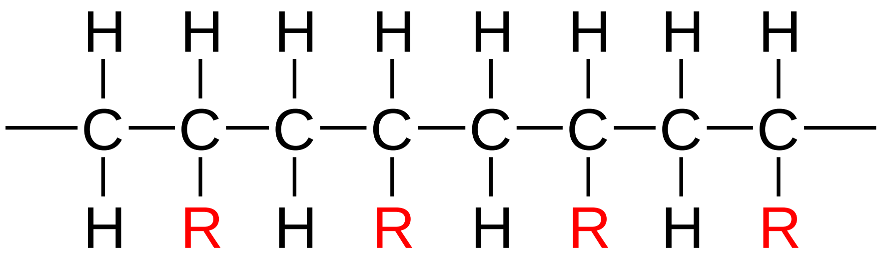
Stereoisomerism



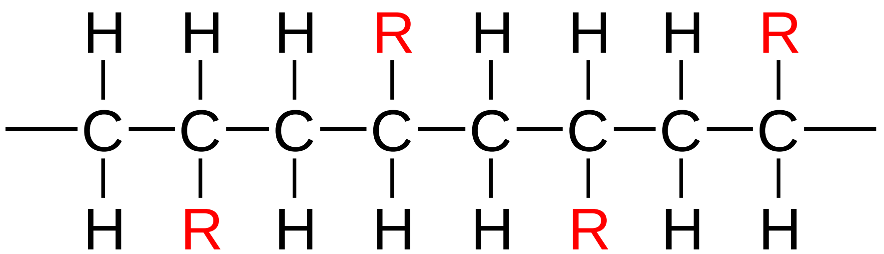
# Tacticity

Tacticity – stereoregularity of chain

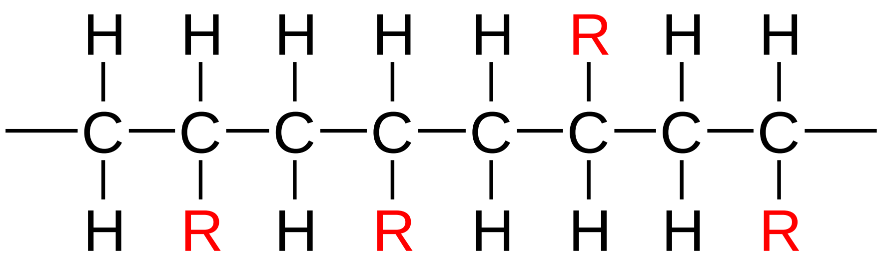
- Isotactic – all R groups on same side of chain



- Syndiotactic – R groups alternate sides



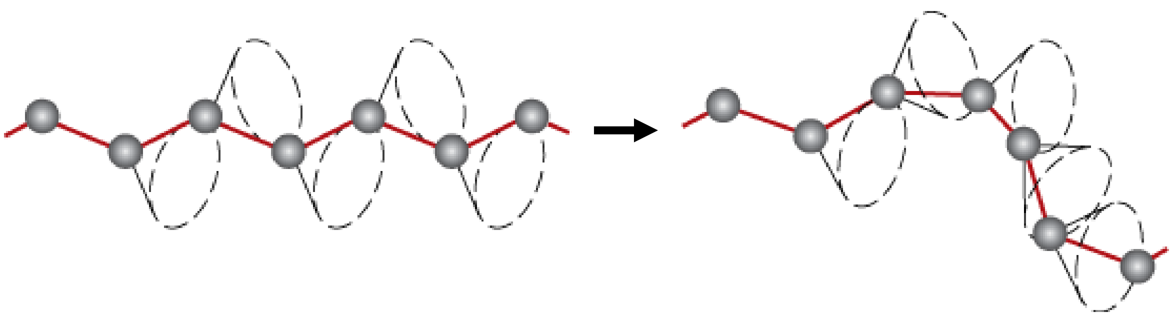
- Atactic – R groups random

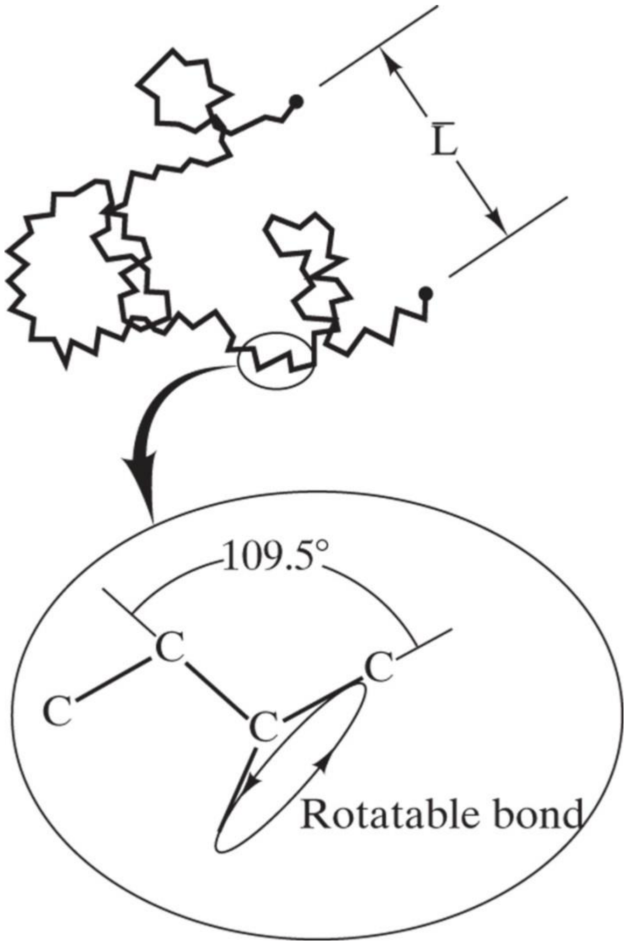


# Polymers – Molecular Shape

Conformation – Molecular orientation can be changed by rotation around the bonds

- note: no bond breaking needed





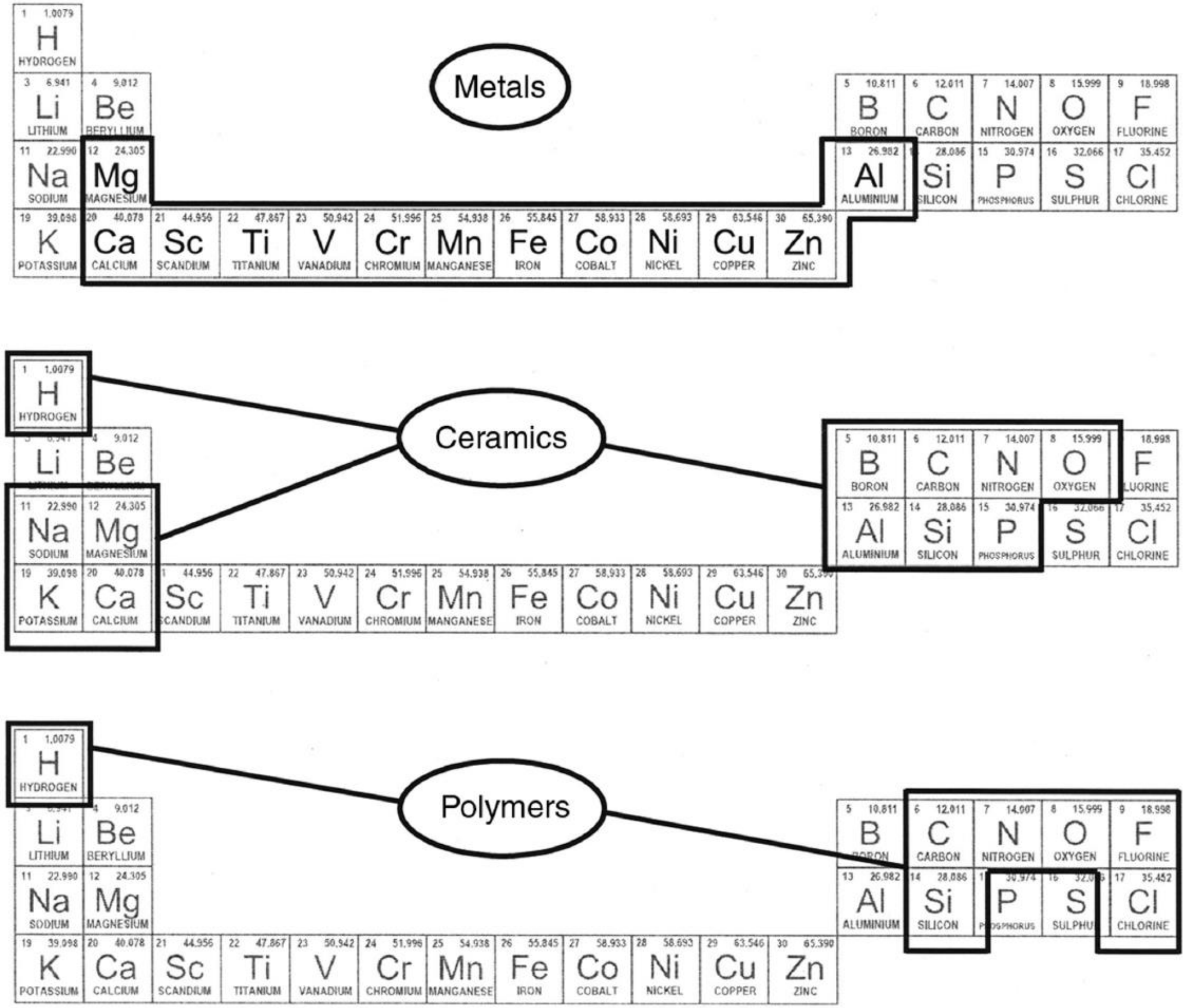
# Polymers: Advantages Vs. Disadvantages

- ✓ Cheap
- ✓ Tough
- ✓ Lightweight: polyethylene density = 0.96 g cm-3
- ✓ Easy to shape
- ✓ Flexible
- ✓ Resistant to chemical attack
- ✓ Thermally, electrically insulating

**BUT**

- ➢ low stiffness / strength: E (polyethylene) = 1 GPa
- ➢ limited temperature range: Tm (polyethylene) = 105°C
- ➢ high coefficient of thermal expansivity: a (polyethylene) = 150 x 10-6 K-1
- ➢ Degrade when exposed to UV light, oxygen

# Periodic Table: metals, ceramics and polymers



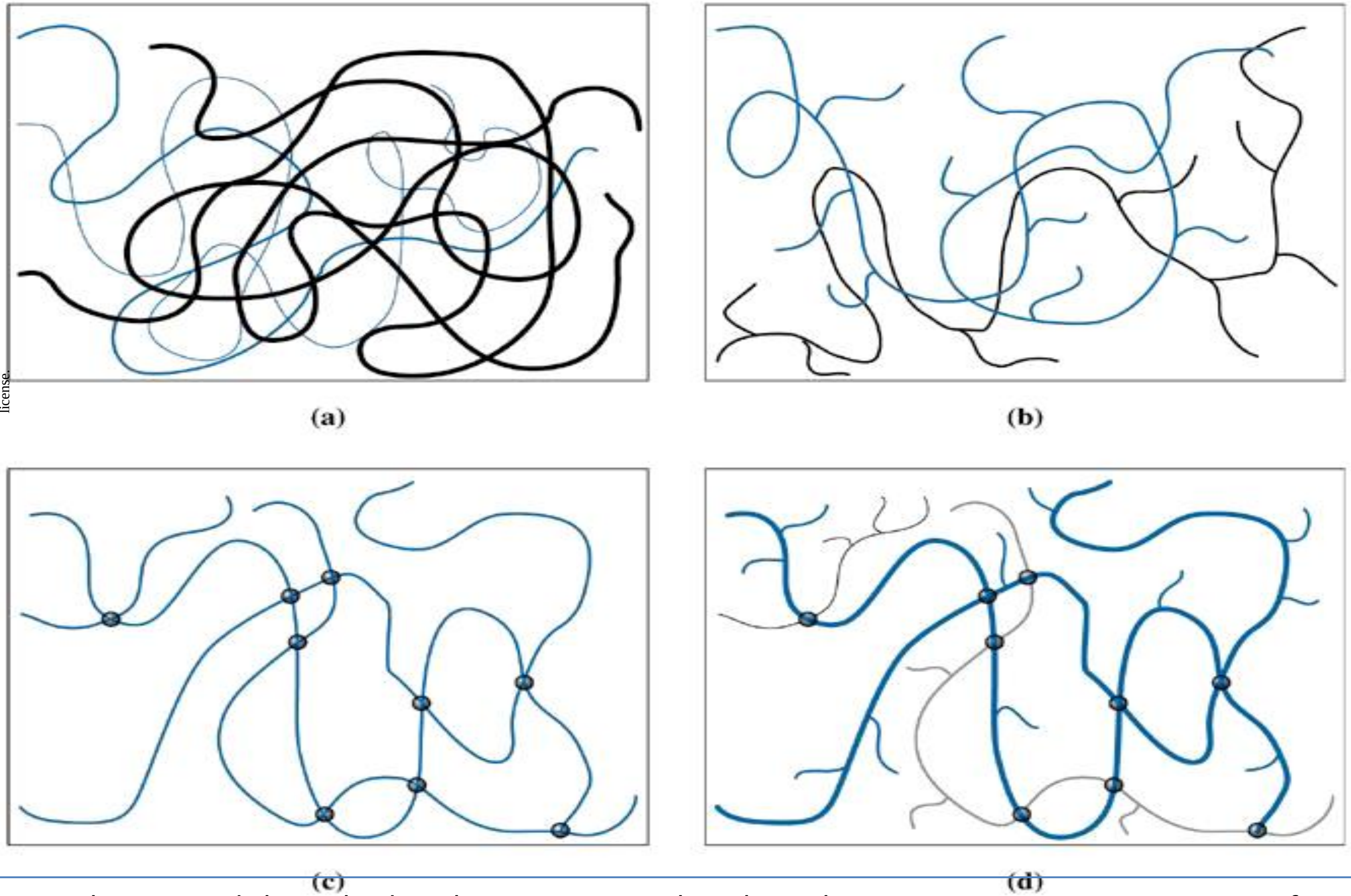
# Classification of polymers

- Linear polymer - Any polymer in which molecules are in the form of spaghetti-like chains.

- Thermoplastics - Linear or branched polymers in which chains of molecules are not interconnected to one another.

- Thermosetting polymers - Polymers that are heavily cross-linked to produce a strong three dimensional network structure.

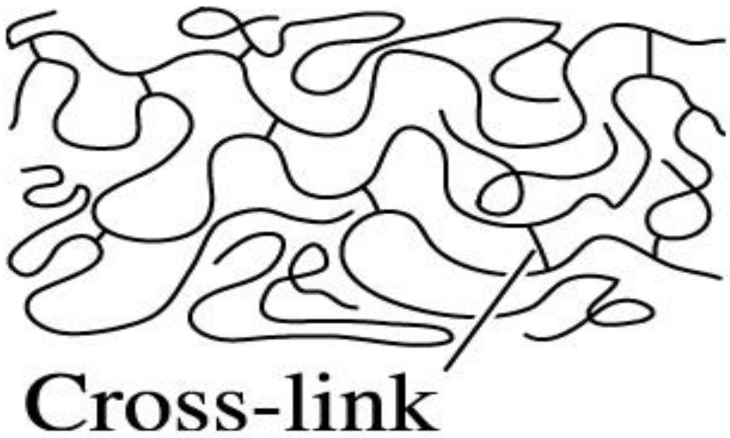
- Elastomers - These are polymers (thermoplastics or lightly cross-linked thermosets) that have an elastic deformation > 200%.



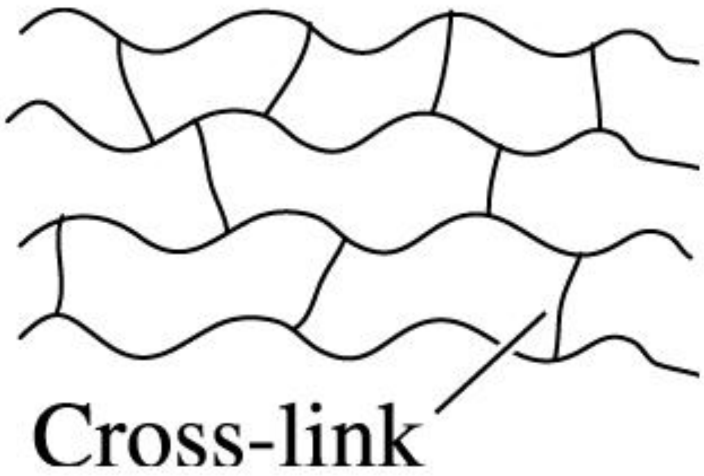



Schematic showing linear and branched polymers. Note that branching can occur in any type of polymer (e.g., thermoplastics, thermosets, and elastomers). **(a)** Linear unbranched polymer: notice chains are not straight lines and not connected. Different polymer chains are shown using different shades and design to show clearly that each chain is not connected to another. **(b)** Linear branched polymer: chains are not connected, however they have branches. **(c)** Thermoset polymer without branching: chains are connected to one another by covalent bonds but they do not have branches. Joining points are highlighted with solid circles, **(d)** Thermoset polymer that has branches and chains that are interconnected via covalent bonds. Different chains and branches are shown in different shades for better contrast. Places where chains are actually chemically bonded are shown with filled circles.

# Degree of Crosslinking





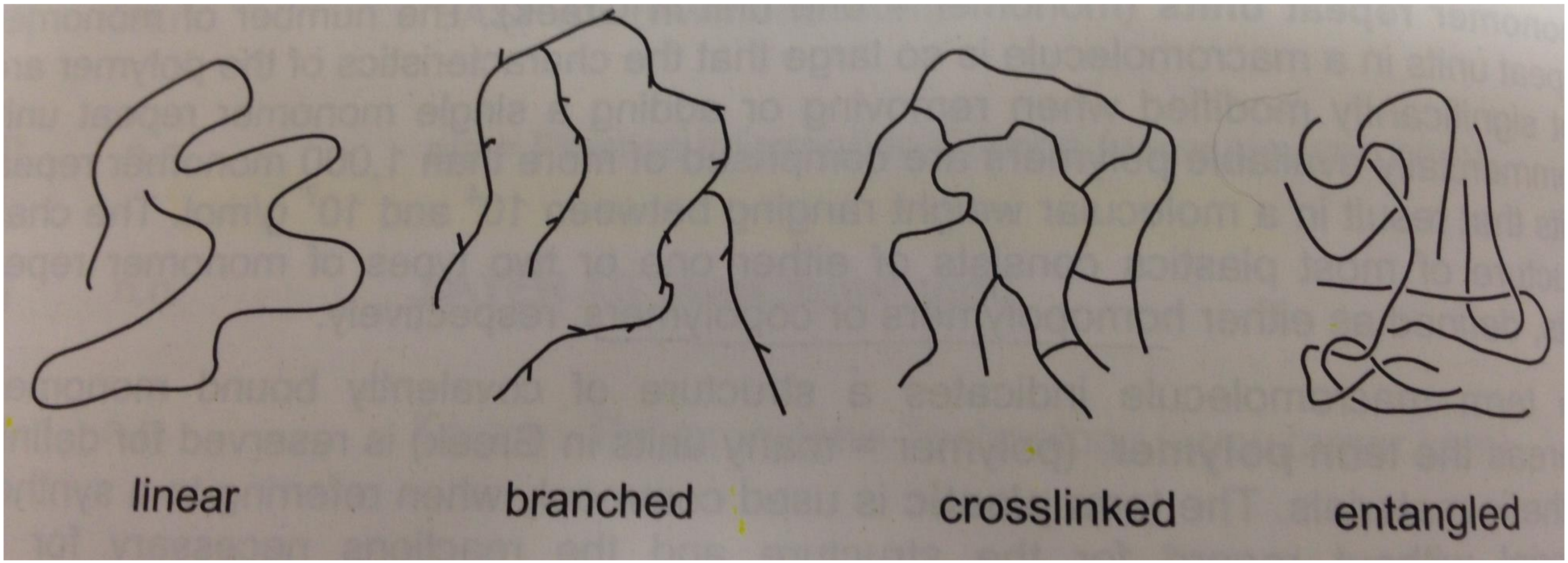






***Comparison of the three polymer categories***

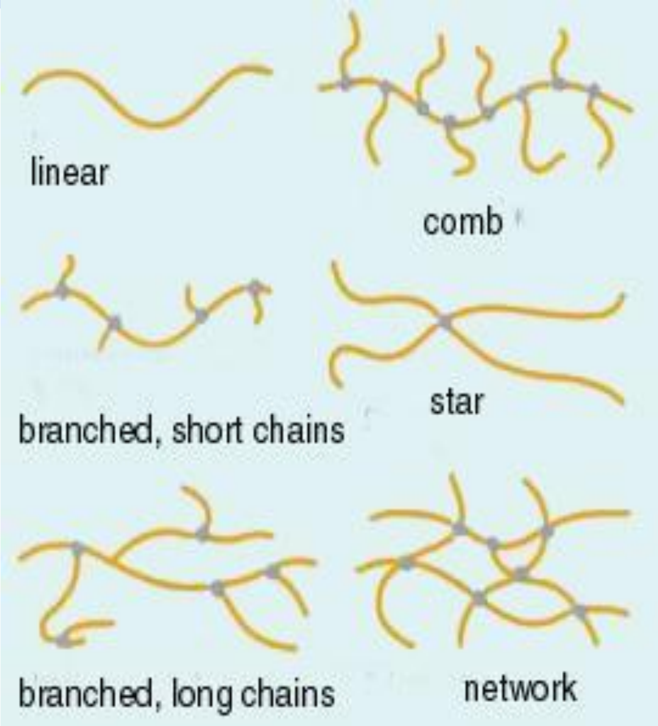
| Behavior | General Structure | Example |
|---|---|---|
| Thermoplastic | Flexible linear chains (straight or branched) | Polyethylene |
| Thermosetting | Rigid three-dimensional network (chains may be linear or branched) | Polyurethanes |
| Elastomers | Thermoplastics or lightly cross-linked thermosets, consist of spring-like molecules | Natural rubber |

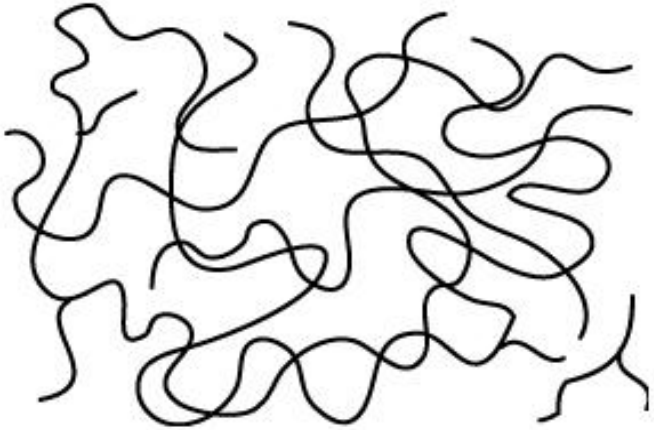
# Chains Shape



# Entanglement: Physical Bonding

- Plastic material can be envisioned as a plate of spaghetti. You have very long molecules which get entangled with each other as they try to move.
- This entanglement holds the material together along with secondary forces.
- Chemical Bonding forces are up to $10^3$ times stronger than physical bonding.
- Entanglement is why plastics burn before they enter a gaseous form
- Plastic molecules do not share primary bonds with the adjacent plastic molecules. If they did, they would be cross-linked and depending on the degree of cross linking, would not re-melt when re-heated
- Side groups and secondary forces can greatly increase the entanglement forces and thereby increase the viscosity of the material



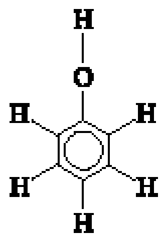
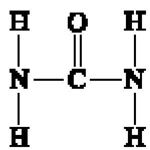
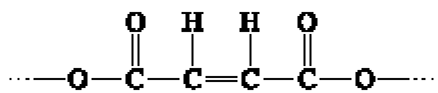
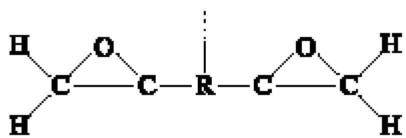
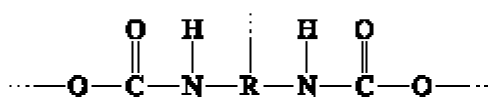
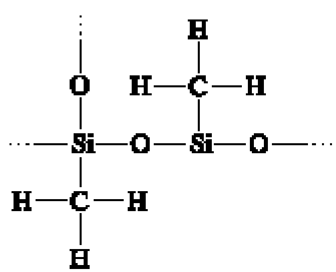
# Thermoplastics and Thermosets

- The response of a polymer to mechanical forces at elevated temperature is related to its dominant molecular structure.
- One classification of polymers is according to its behavior and rising temperature. Thermoplastics and Thermosets are the 2 categories.
- A thermoplastic is a polymer that turns to a liquid when heated and freezes to a very glassy state when cooled sufficiently.
- Thermoplastics consist of a large number of **independent** and **intertwined molecular chains**
- Thermoplastic polymers differ from thermosetting polymers (Bakelite, vulcanized rubber) since thermoplastics can be remelted and remolded.
- **Thermosetting plastics** when heated, will chemically decompose, so they can not be recycled. Yet, once a thermoset is cured it tends to be stronger than a thermoplastic.
- **Crosslinking density of thermoset**= 1 crosslinking point per 20 carbon atoms on the backbone.
- Typically, linear polymers with minor branched structures (and flexible chains) are thermoplastics. The networked structures are thermosets.

# Examples of Thermoplastics

| | Tensile Strength (psi) | % Elongation | Elastic Modulus (psi) | Density ($g/cm^3$) | Izod Impact (ft lb/in.) |
|---|---|---|---|---|---|
| Polyethylene (PE): | | | | | |
| Low-density | 3,000 | 800 | 40,000 | 0.92 | 9.0 |
| High-density | 5,500 | 130 | 180,000 | 0.96 | 4.0 |
| Ultrahigh molecular weight | 7,000 | 350 | 100,000 | 0.934 | 30.0 |
| Polyvinyl chloride (PVC) | 9,000 | 100 | 600,000 | 1.40 | |
| Polypropylene (PP) | 6,000 | 700 | 220,000 | 0.90 | 1.0 |
| Polystyrene (PS) | 8,000 | 60 | 450,000 | 1.06 | 0.4 |
| Polyacrylonitrile (PAN) | 9,000 | 4 | 580,000 | 1.15 | 4.8 |
| Polymethyl methacrylate (PMMA) (acrylic, Plexiglas) | 12,000 | 5 | 450,000 | 1.22 | 0.5 |
| Polychlorotrifluoroethylene | 6,000 | 250 | 300,000 | 2.15 | 2.6 |
| Polytetrafluoroethylene (PTFE, Teflon) | 7,000 | 400 | 80,000 | 2.17 | 3.0 |
| Polyoxymethylene (POM) (acetal) | 12,000 | 75 | 520,000 | 1.42 | 2.3 |
| Polyamide (PA) (nylon) | 12,000 | 300 | 500,000 | 1.14 | 2.1 |
| Polyester (PET) | 10,500 | 300 | 600,000 | 1.36 | 0.6 |
| Polycarbonate (PC) | 11,000 | 130 | 400,000 | 1.20 | 16.0 |
| Polyimide (PI) | 17,000 | 10 | 300,000 | 1.39 | 1.5 |
| Polyetheretherketone (PEEK) | 10,200 | 150 | 550,000 | 1.31 | 1.6 |
| Polyphenylene sulfide (PPS) | 9,500 | 2 | 480,000 | 1.30 | 0.5 |
| Polyether sulfone (PES) | 12,200 | 80 | 350,000 | 1.37 | 1.6 |
| Polyamide-imide (PAI) | 27,000 | 15 | 730,000 | 1.39 | 4.0 |

# Examples of Thermoset

| Polymer | Functional Units | Typical Applications |
|---|---|---|
| Phenolics |  | Adhesives, coatings, laminates |
| Amines |  | Adhesives, cookware, electrical moldings |
| Polyesters |  | Electrical moldings, decorative laminates, polymer matrix in fiberglass |
| Epoxies |  | Adhesives, electrical moldings, matrix for composites |
| Urethanes |  | Fibers, coatings, foams, insulation |
| Silicone |  | Adhesives, gaskets, sealants |

# Elastomers

- Elastomers, often referred to as rubber, can be a thermoplastic or a thermoset depending on the structure.
- Crosslinking density= 1 crosslinking point per 1000 carbon atoms on the backbone.
- They are excellent for parts requiring flexibility, strength and durability: such as automotive and industrial seals, gaskets and molded goods, roofing and belting, aircraft and chemical processing seals, food, pharmaceutical and semiconductor seals, and wire and cable coatings.

| | Tensile Strength (psi) | % Elongation | Density ($g/cm^3$) |
|---|---|---|---|
| Polyisoprene | 3000 | 800 | 0.93 |
| Polybutadiene | 3500 | | 0.94 |
| Polyisobutylene | 4000 | 350 | 0.92 |
| Polychloroprene (Neoprene) | 3500 | 800 | 1.24 |
| Butadiene-styrene (BS or SBR rubber) | 3000 | 2000 | 1.0 |
| Butadiene-acrylonitrile | 700 | 400 | 1.0 |
| Silicones | 1000 | 700 | 1.5 |
| Thermoplastic elastomers | 5000 | 1300 | 1.06 |

# Elastomeric Materials

- In comparison with thermoset, most elastomers have lower crosslink density.

- Common characteristics;

  - ✓ Large elastic elongation (i.e.200%)
  - ✓ Can be stretched and then immediately return to their original length when the load was released

- All materials have some elastic elongation

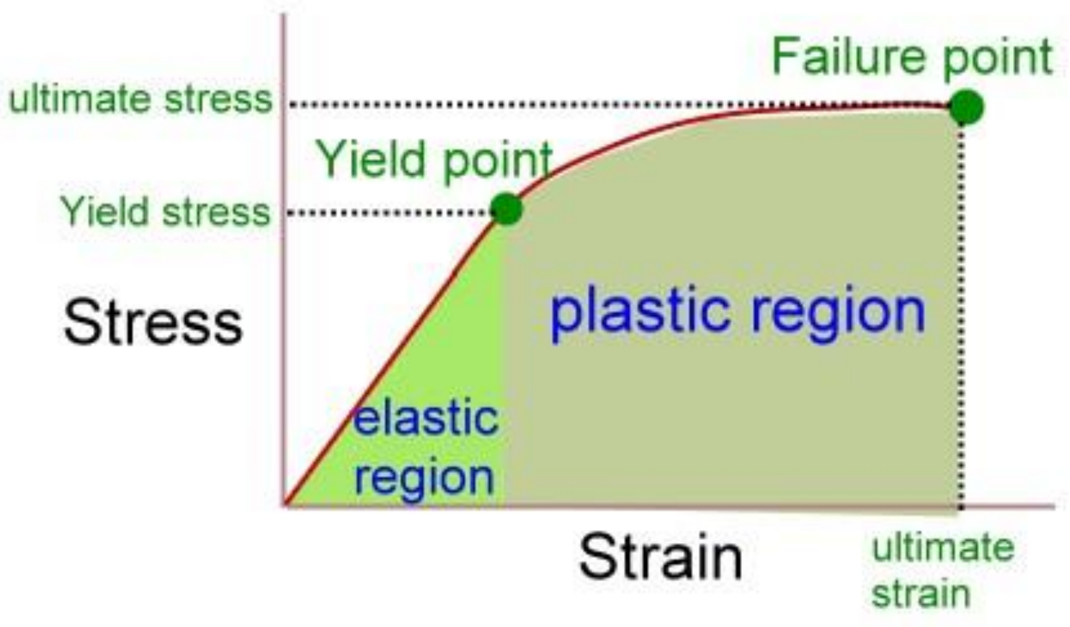
  - ➢ "elastic elongation = elongation of any material when that material is at its yield point"
  - ➢ Ceramic & metal- small elastic elongation; 2%
  - ➢ PE, elastic elongation; 50%

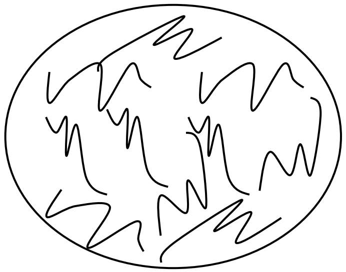
- Elastomers are sometimes called rubber or rubbery materials

- The term elastomer is often used interchangeably with the term rubber

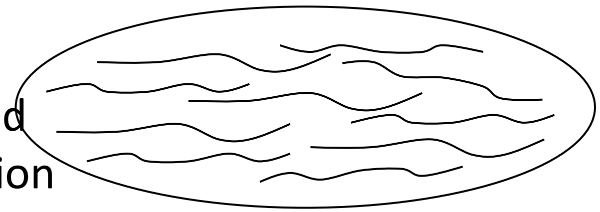
- Elastomers are usually thermosets (requiring vulcanization) but may also be thermoplastic.

# Stress-Strain: Elastic region



No Stress



Stressed
In tension

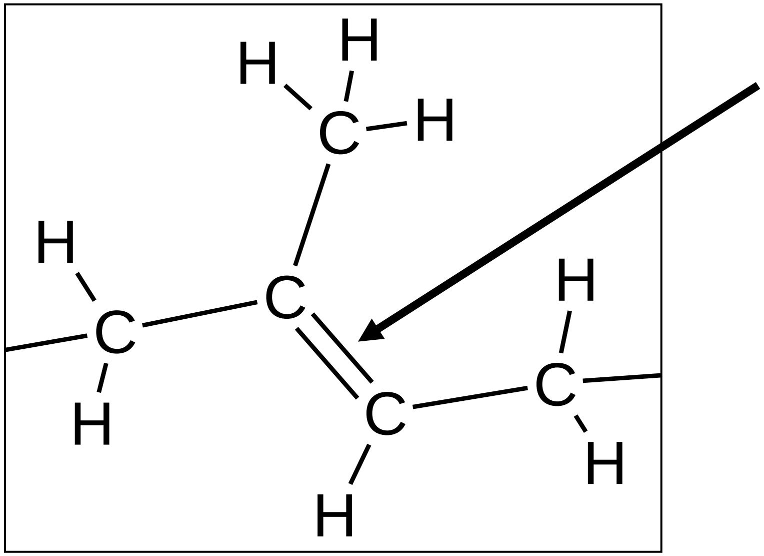
# Elasticity

**Rubber > LLPDE > Epoxy Strip**

# Natural Rubber

- Rubber tree (Hevea Braziliensis)
- Natural rubber is obtained by drying a latex rubber (milk in which the butter fat component is suspended in water salution)
- High temperature stability – cooking the crude natural rubber with sulphur (vulcanization)
- Vulcanization creates crosslinking between rubber molecules
- Natural rubber is highly elastomeric (elongation 1000% for vulcanized natural rubber)
- Compared to other elastomeric materials, natural rubber shows higher tensile strength, high tear strength, high resilience, resistance to wear, etc

- Discovered that the polymer could be crosslinked (cured or vulcanized) by heating with sulphur,
- Crude natural rubber was chiefly composed of cis-polyisoprena (a polymer chain with carbon carbon double bond with repeating unit)



Sulphur attacks this double bond

- As many as 8 sulphur atoms might be in the bridge between molecules

# Thermoplastic Elastomers (TPE)

- The chains of TPEs are physically bonded and entangled.
- These materials are not crosslinked, have some distinct processing advantages over traditional thermoset elastomers and physical properties of vulcanized elastomers
- At ambient temperatures TPEs behave like conventional crosslinked rubbers but they have the additional advantage that their thermal behavior is reversible
- TPEs are able to be molded like thermoplastic (injection molding, extrusion, etc)
- Thermoplastic elastomers are more temperature sensitive
- Scrap and reject of these materials can be recycled-environmental friendly behavior
- Normal crosslinked polymers cannot be recycled because they don't melt. They don't melt because the crosslinks tie all the polymer chains together, making it impossible for the material to flow.

# TPE: Styrene-Butadiene (SB) copolymer