Lecture 25

Materials and their structure- Polymers

Textbooks:

- Introduction to materials science and Engineering: V. Raghavan
- Materials Science and Engineering: Callister and Rethwisch

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Recap…

1. Non-crystalline solids: amorphous solids (glass)
2. Structure of Silicates
3. Supercooling: glass formation
4. Energy landscape of glasses

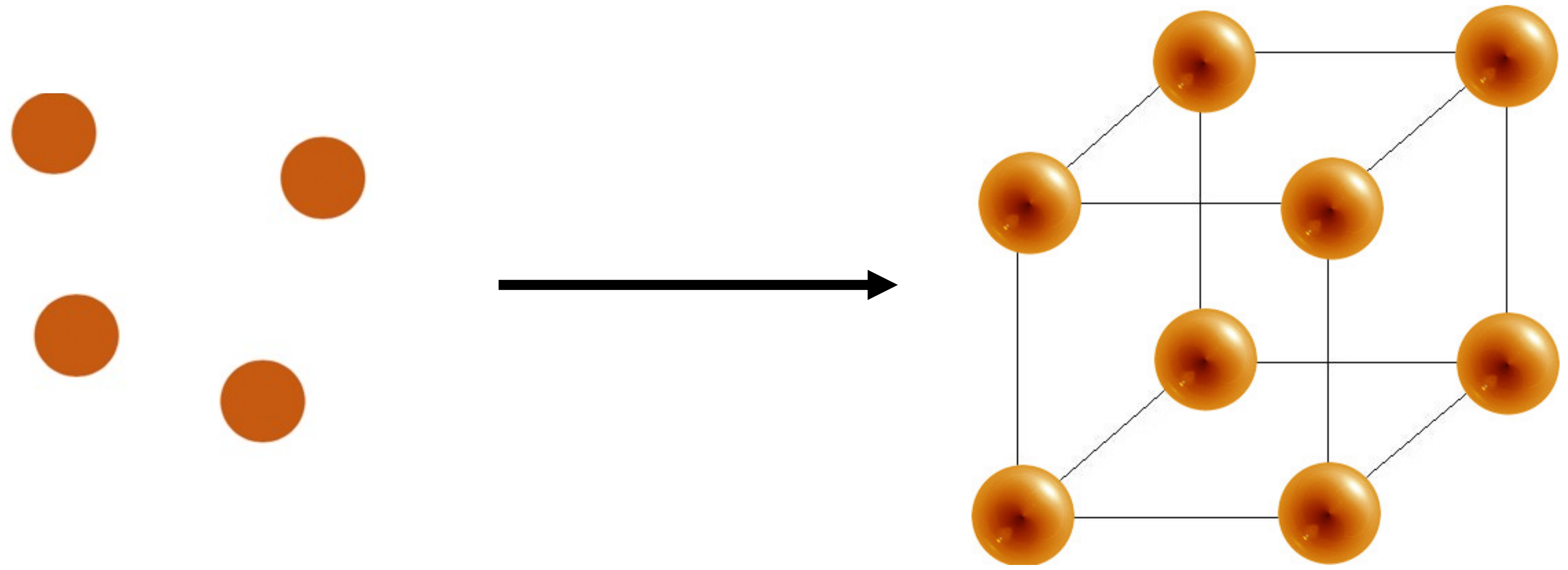
Metals are usually considered more important than wood.. Is that a correct convention?

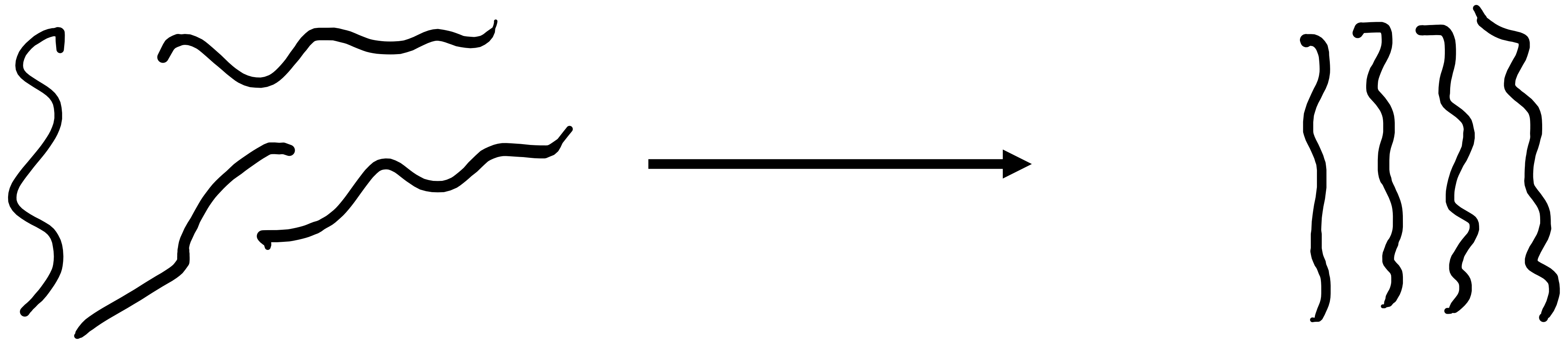
More robust in ice than steel ships

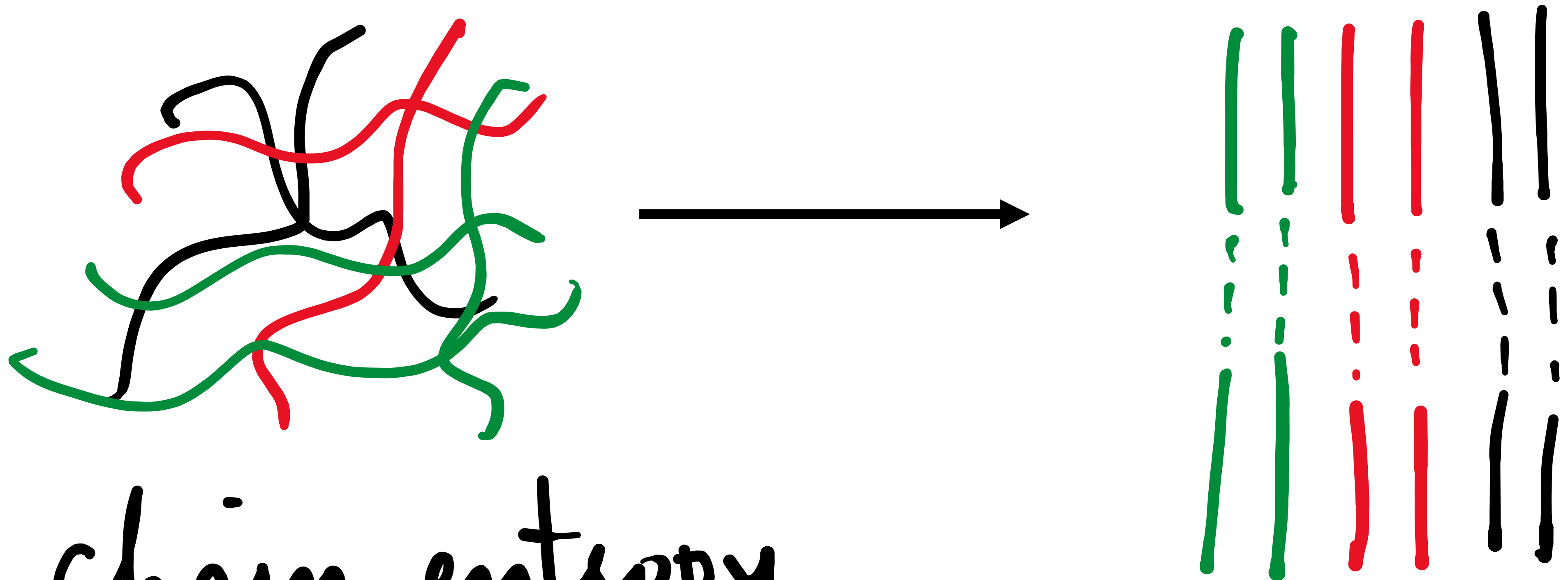
Composed of cellulose: polymer of glucose= SUGAR!
-Strong
- Not brittle

Crystalline sugar is brittle!

What distinguishes polymers from small molecules and oligomers?

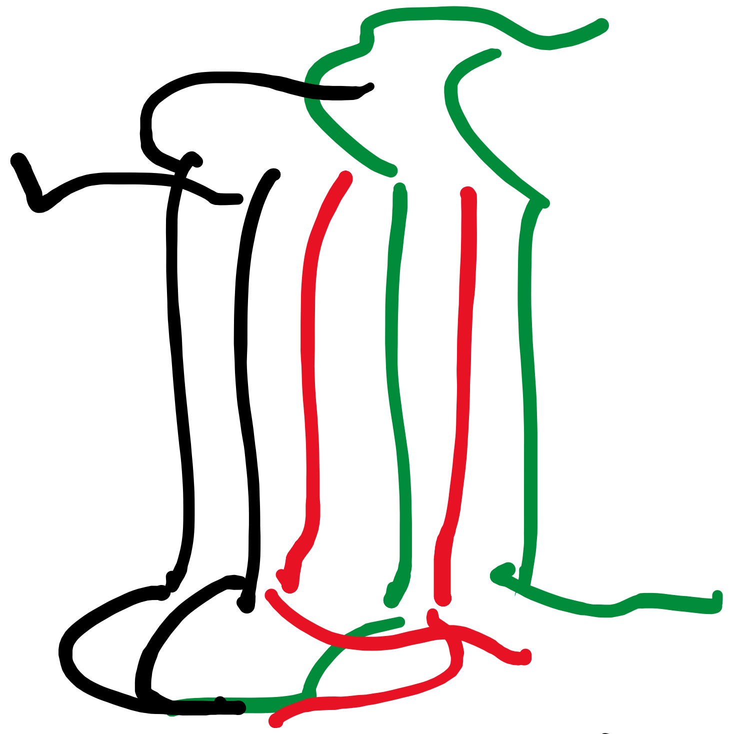






chain entropy

or



(Is TS negligible)

??

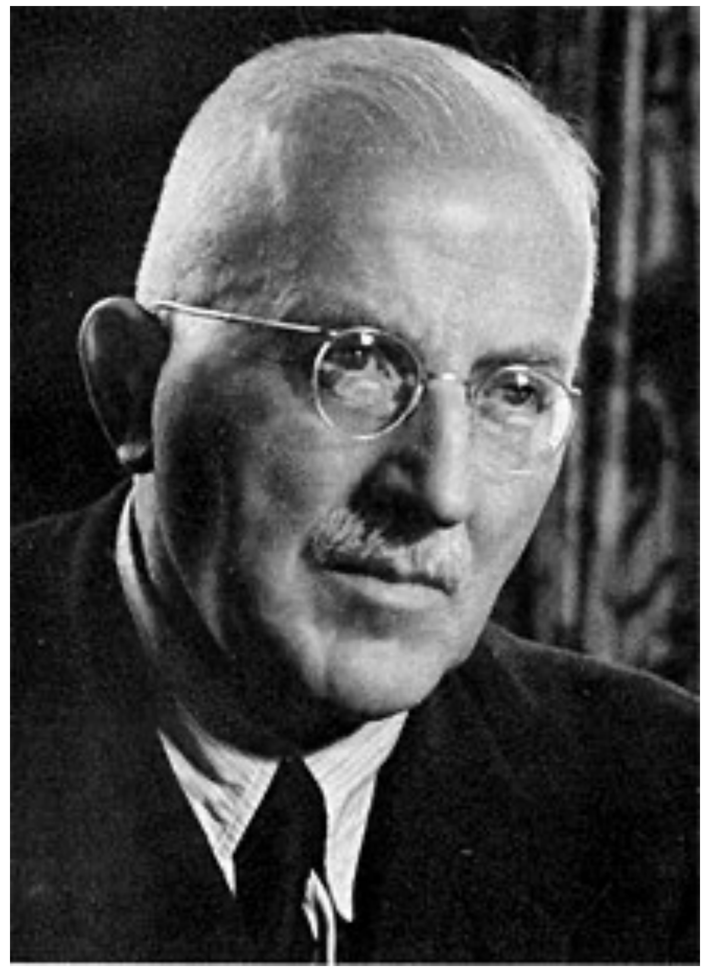
$G = E - TS$

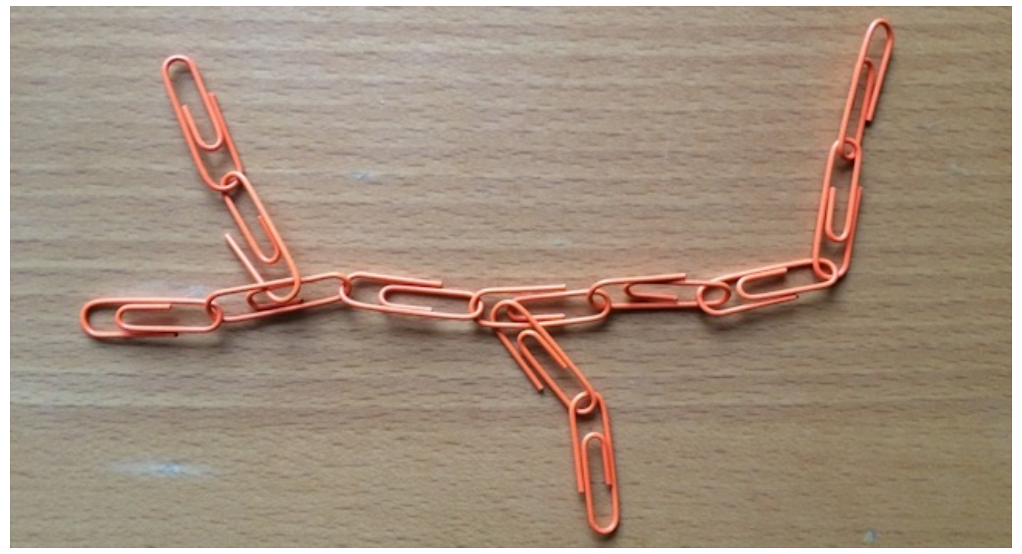
Poly+mer

- Substances composed of molecules of relatively high mass with repeating units. Long chain molecules containing thousand to million atoms
- BIG molecules
- How BIG?
- No. of repeating units: 10+ to 10^6
- Molecular weight: molecular mass X ($6.023X10^{23}$)
- Polymers are mixtures: average values are used

Hermann Staudinger

Macromolecular Hypothesis





A polymer model

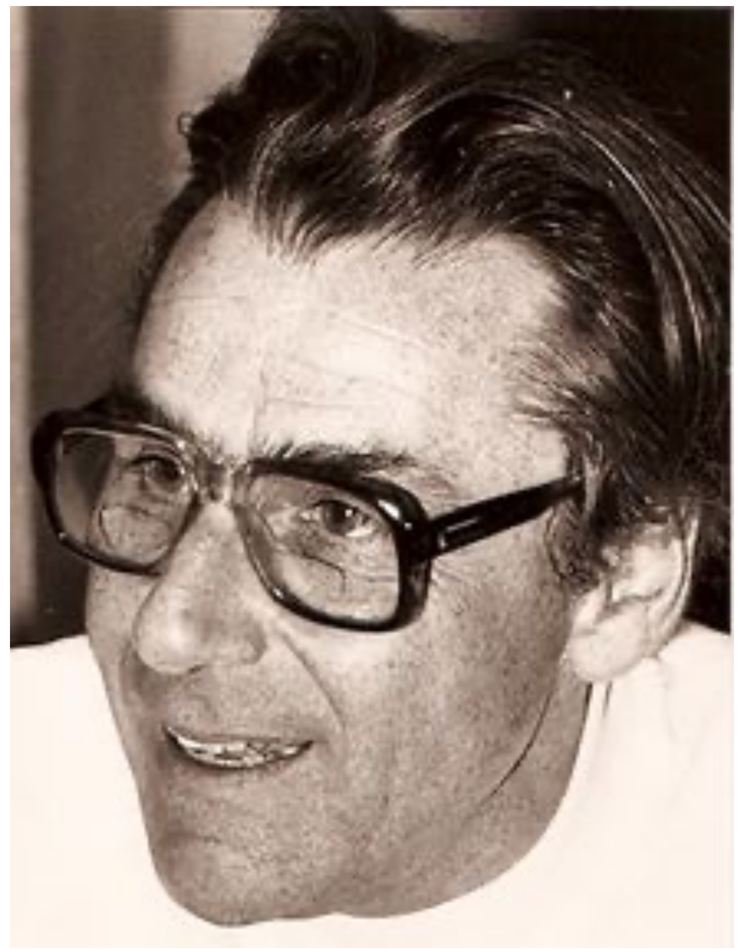
1920:
- Elementary units of polymers called *monomers*
- Colloidal properties of polymers: sizes of macromolecules

1953 Nobel Prize in Chemistry

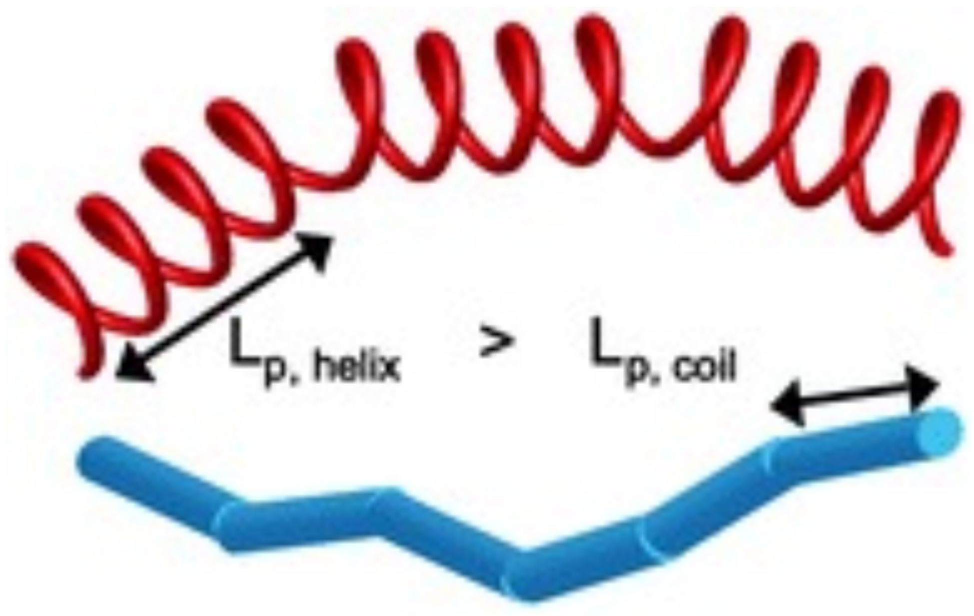
Wikipedia

Hans Kuhn

Macromolecular sizes



-Decoiling of a random coiled chain molecule in a flowing viscous solvent.
- 1943: Polymer molecules were described as chains of statistical chain elements.



Paul Flory

Polymers in solution

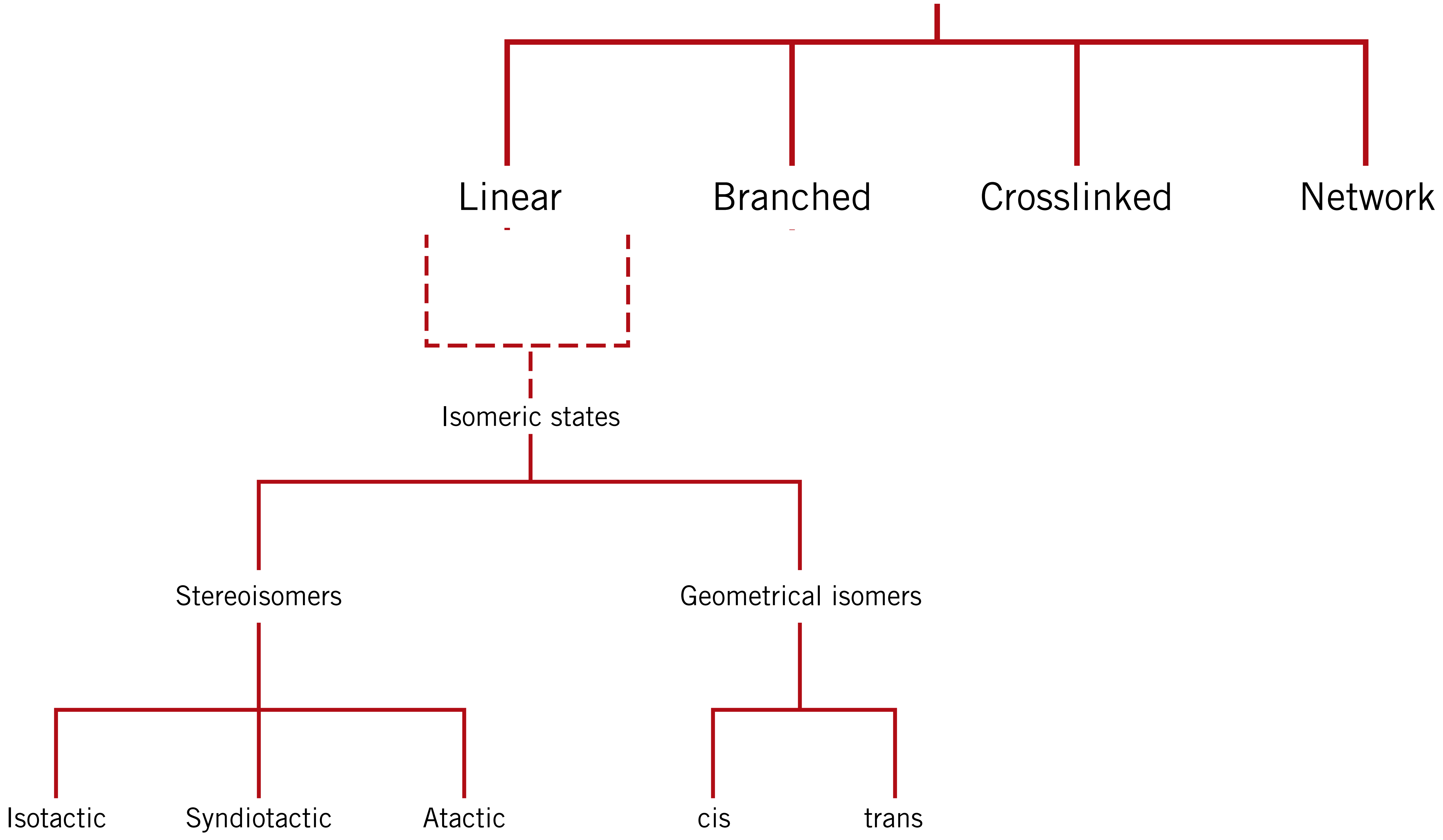
1974 Nobel Prize in Chemistry

-Swelling of a single chain in a good solvent
- Thermodynamics of polymer solutions along with Huggins
- Distribution of molar mass, hydrodynamics

M.L. Huggins: conceived the idea of Hydrogen bonding

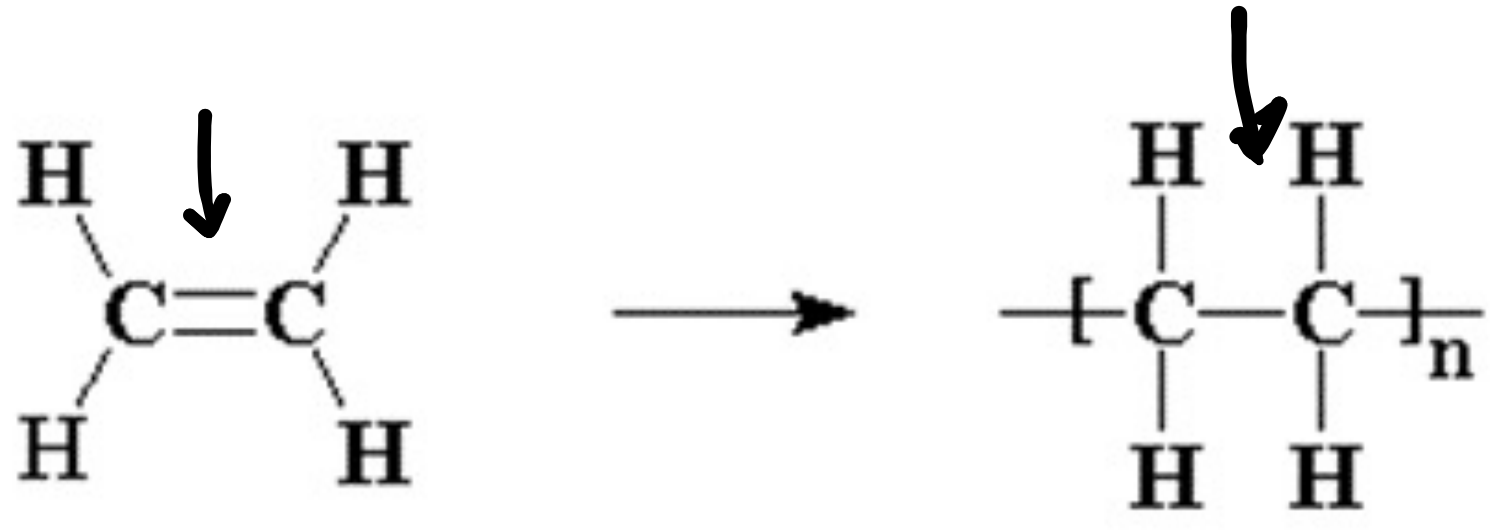
Four main properties

1. Chemistry: monomer
2. Size: molecular Weight and degree of polymerization
3. Shape: chain twisting, entanglement
4. **Structure:** Density and crystallinity



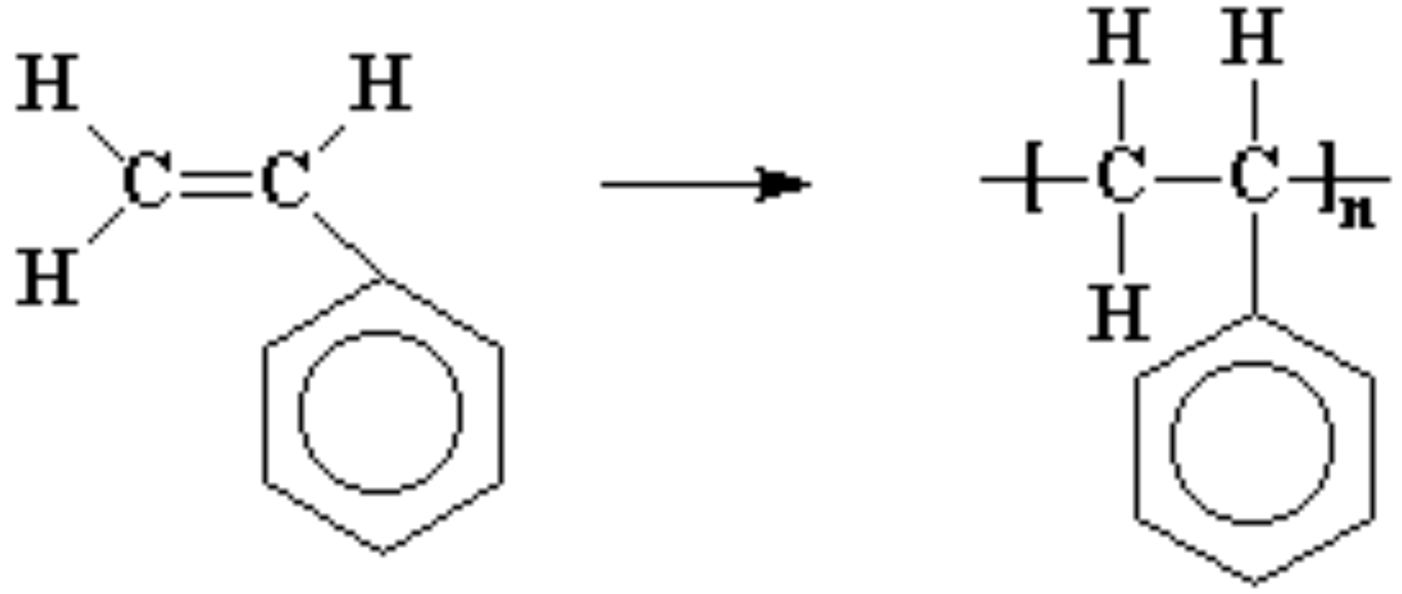
Chemistry of polymers

Monomers of vinyl polymers



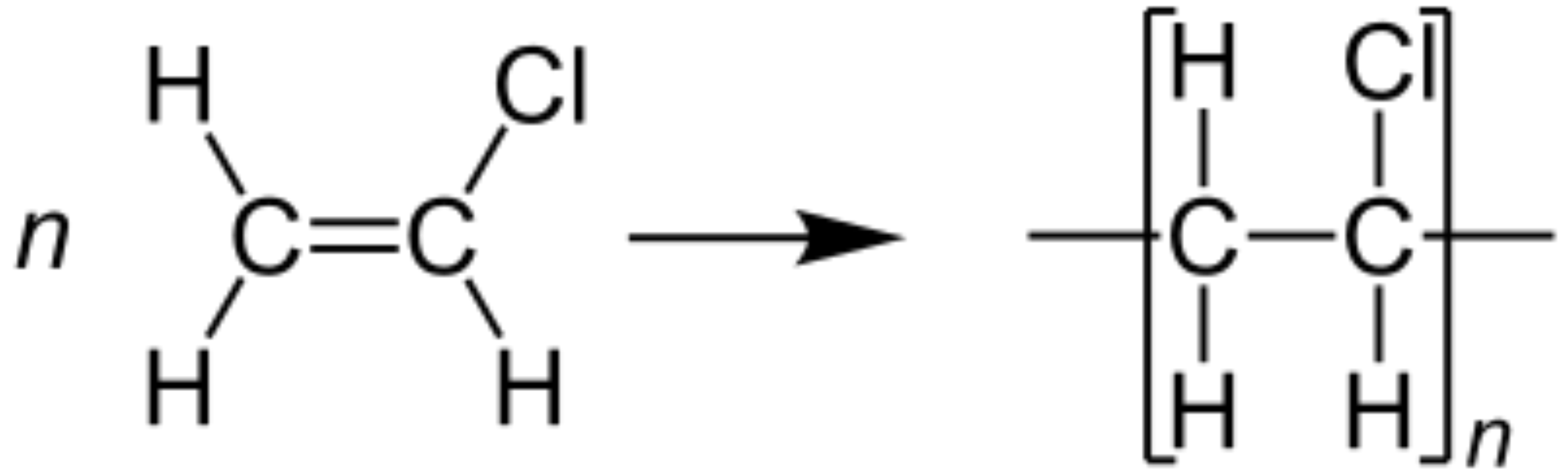
Ethylene

Polyethylene



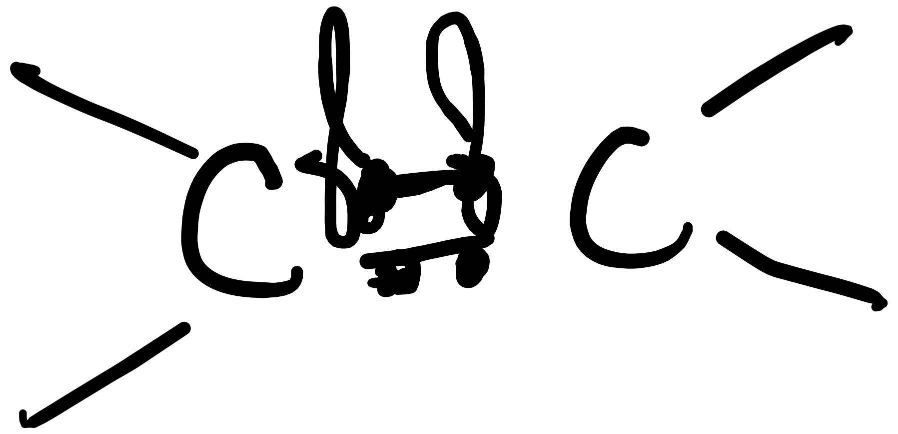
styrene

Polyvinyl styrene

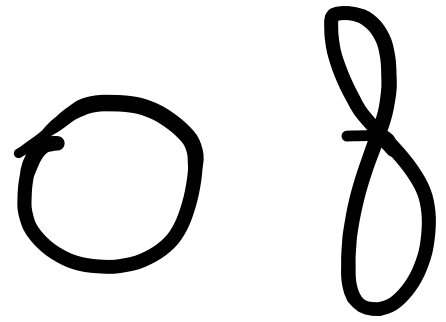


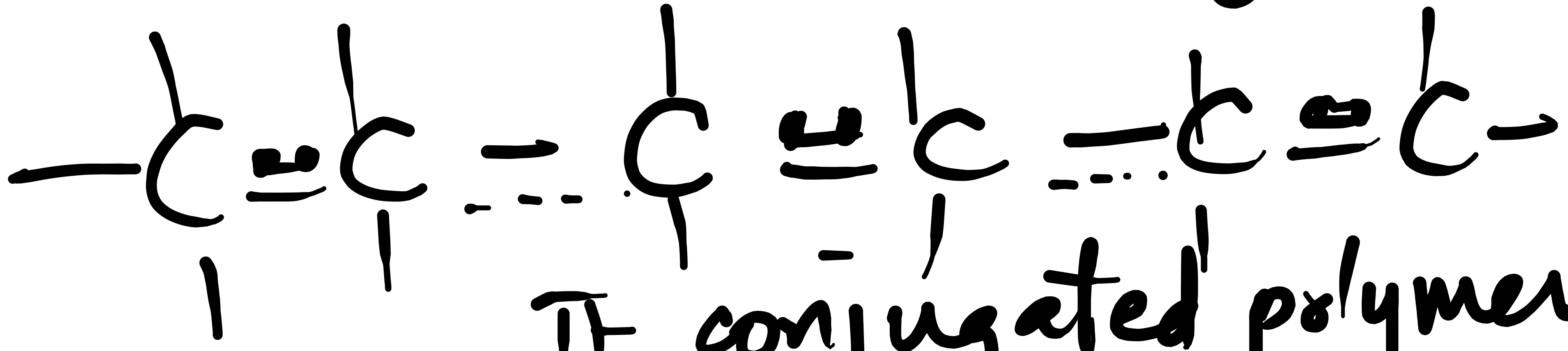
vinyl chloride

Polyvinyl chloride

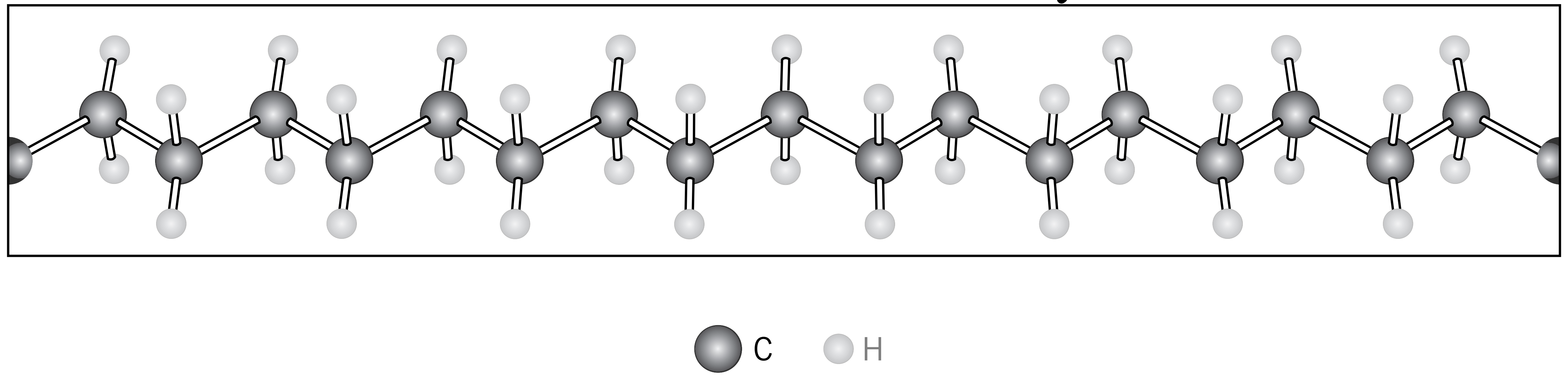


$1\sigma + 1\pi$



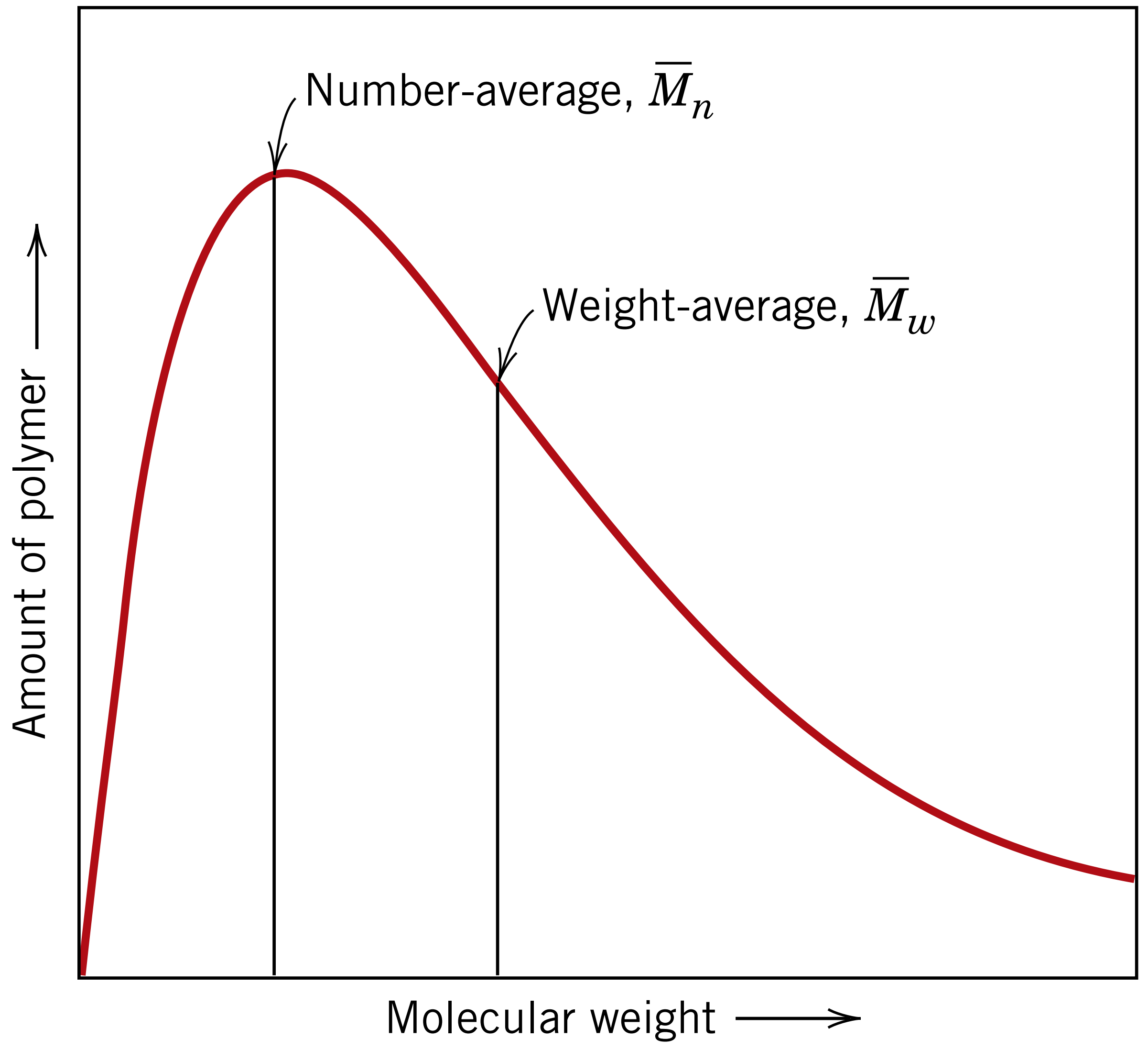


π conjugated polymers



Molecular weight of polymers

Macromolecules



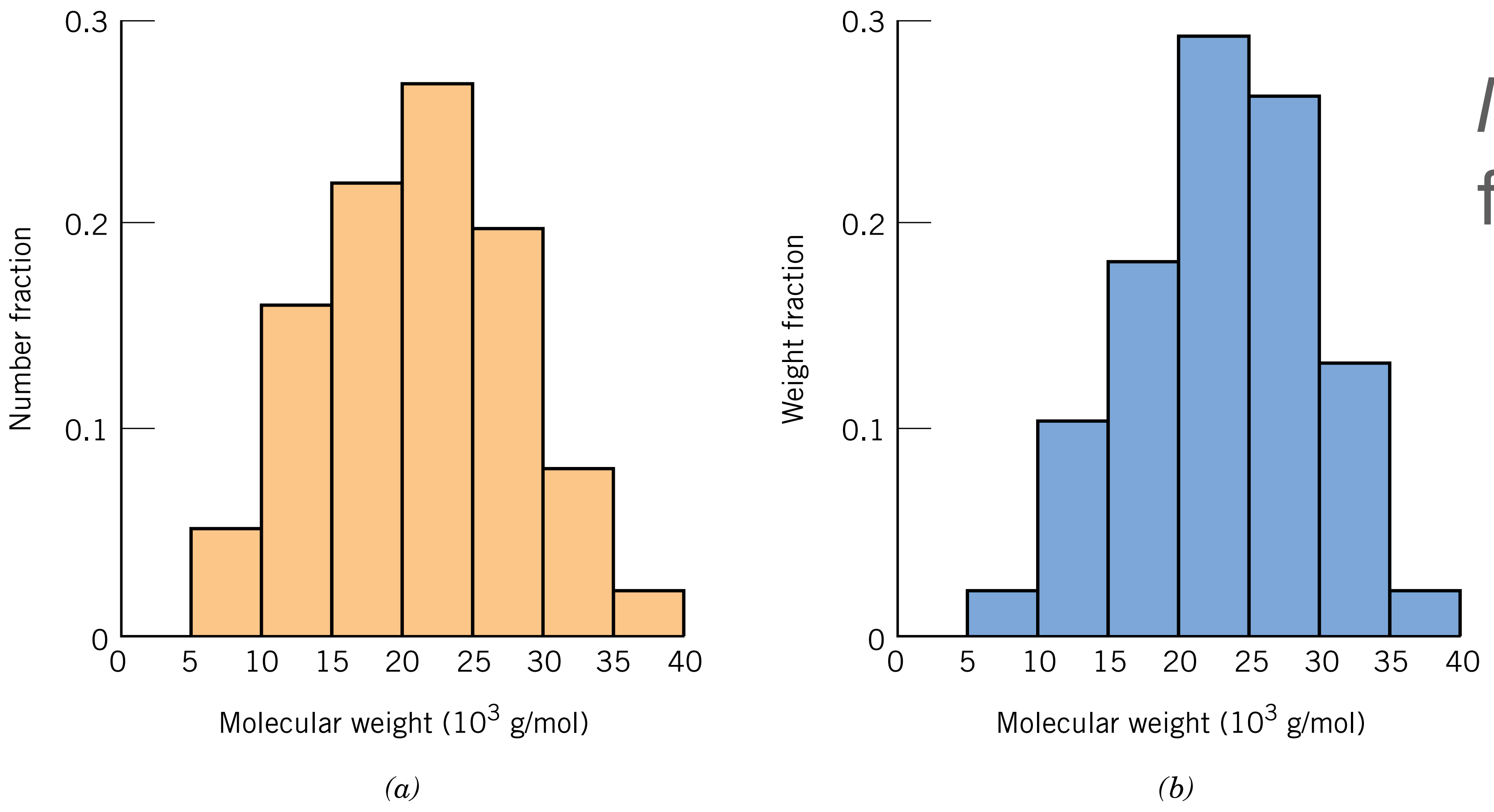
The **number-average molecular weight M_n** is obtained by dividing the chains into a series of size ranges and then determining the number fraction of chains within each size range

$$\overline{M}_n = \Sigma x_i M_i$$

where *Mi* represents the mean (middle) molecular weight of size range *i*, and *xi* is the fraction of the total number of chains within the corresponding size range.

A **weight-average molecular weight *Mw*** is based on the weight fraction of molecules within the various size ranges

$$\overline{M}_w = \Sigma w_i M_i$$



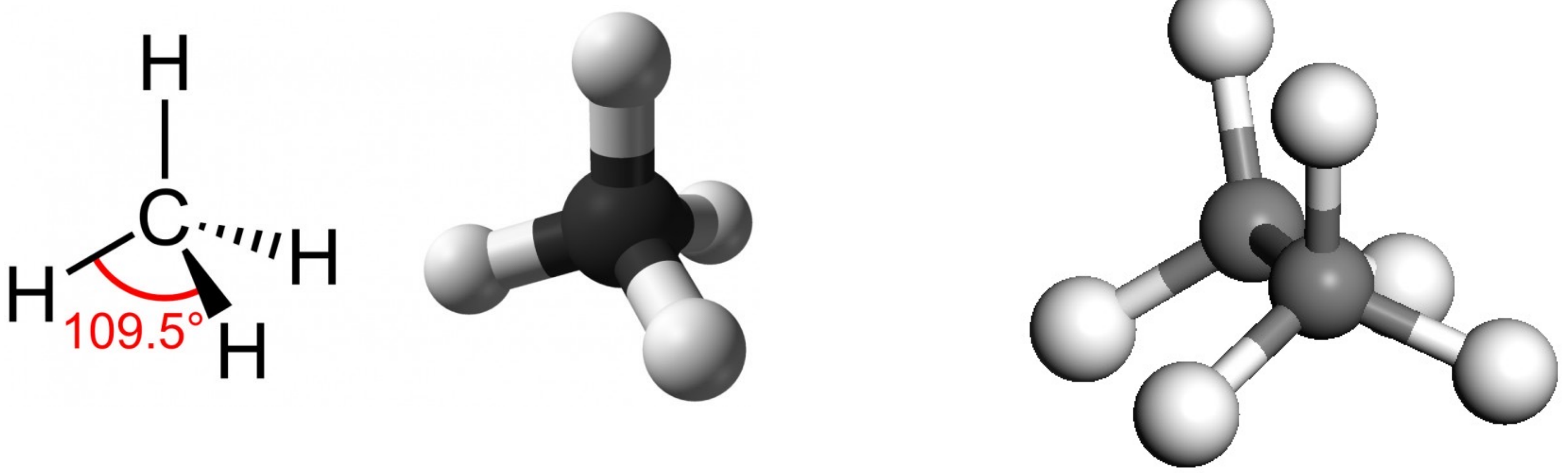
Mi is the mean molecular weight within a size range, whereas *wi* denotes the weight fraction of molecules within the same size interval.

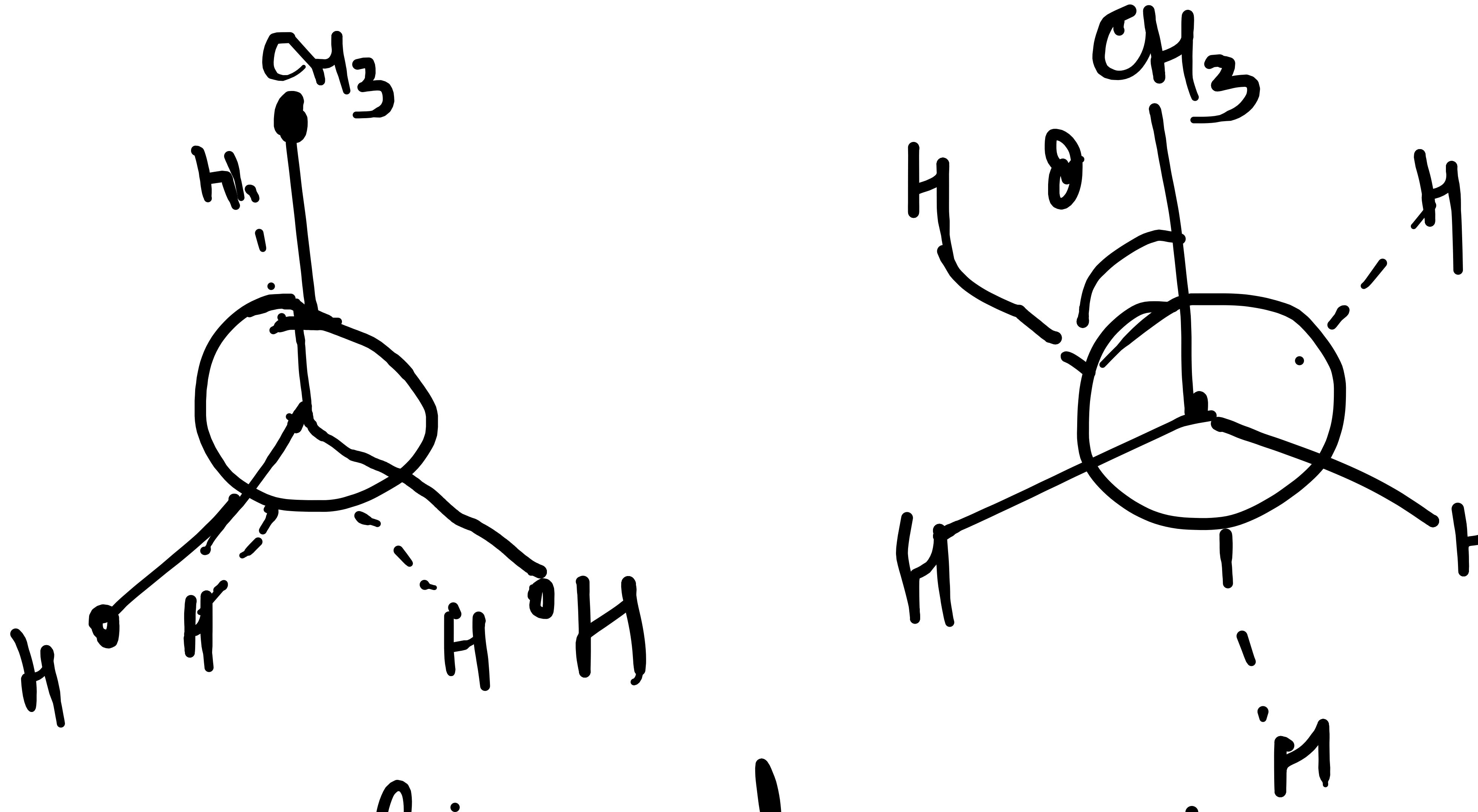
An alternate way of expressing average chain size of a polymer is as the **degree of polymerization**, *DP*, which represents the average number of repeat units of chain. The relationship between DP and number-average molecular weight is

$$DP = \frac{\overline{M}_n}{m}$$

Callister

Molecular shape of polymers or chain conformations

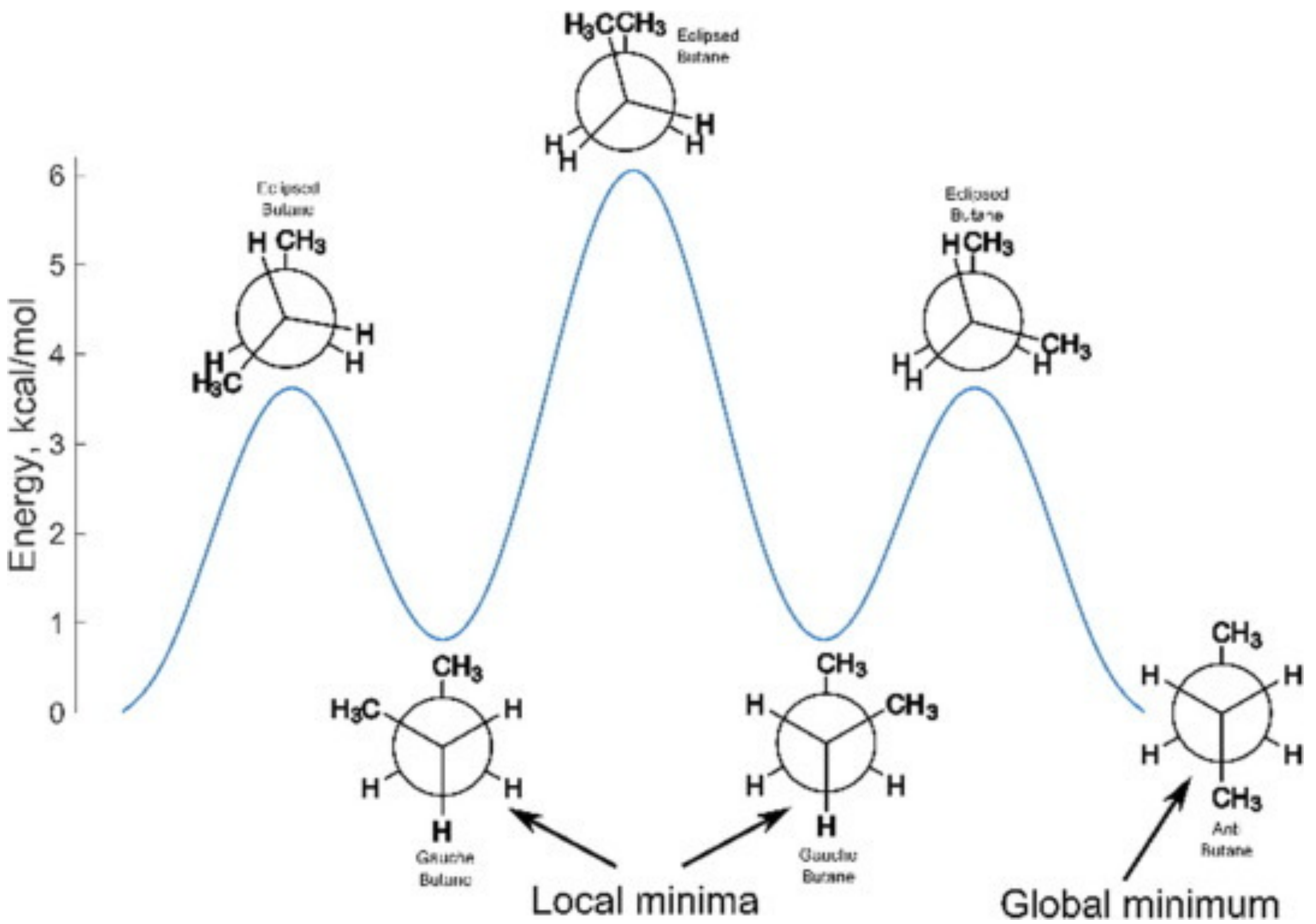




eclipsed   staggered

cis   trans

gauche



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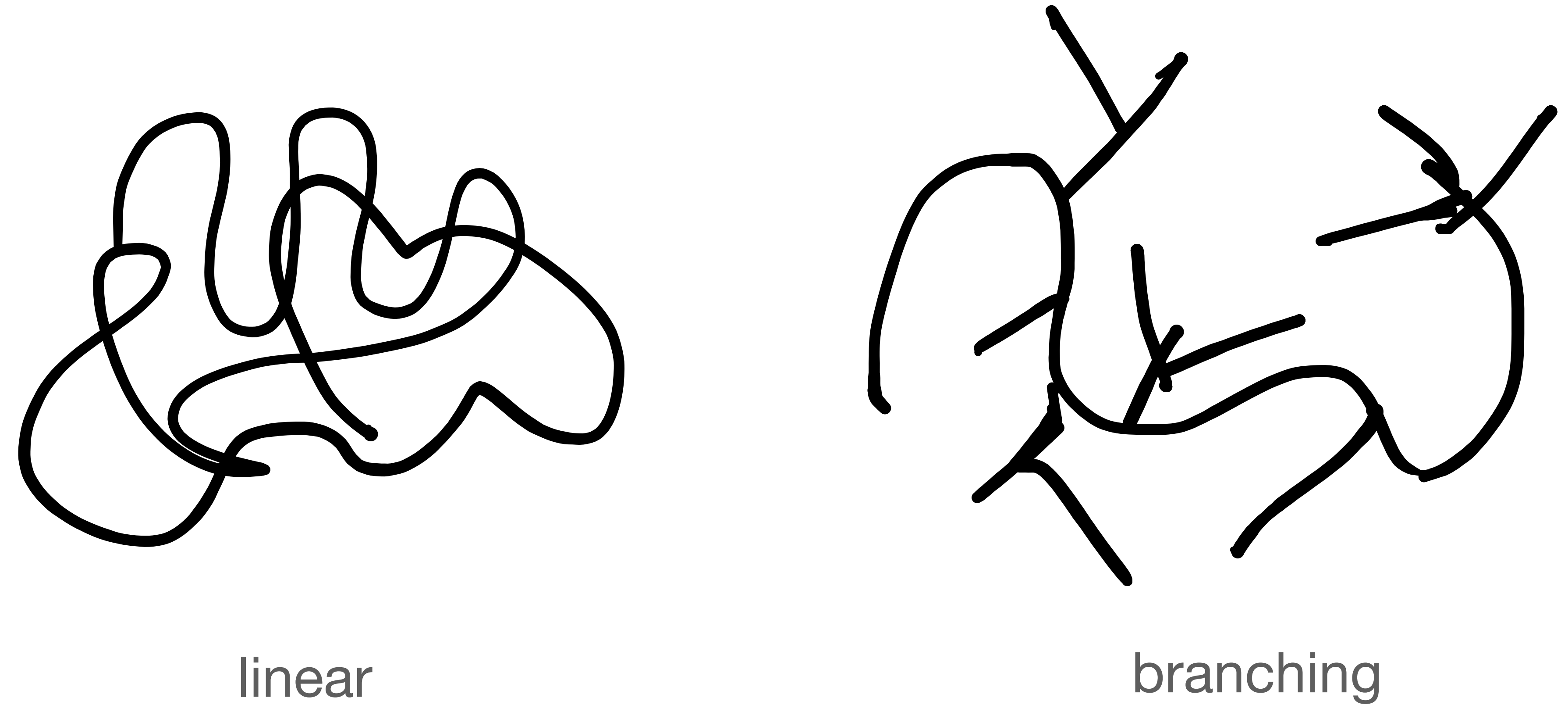
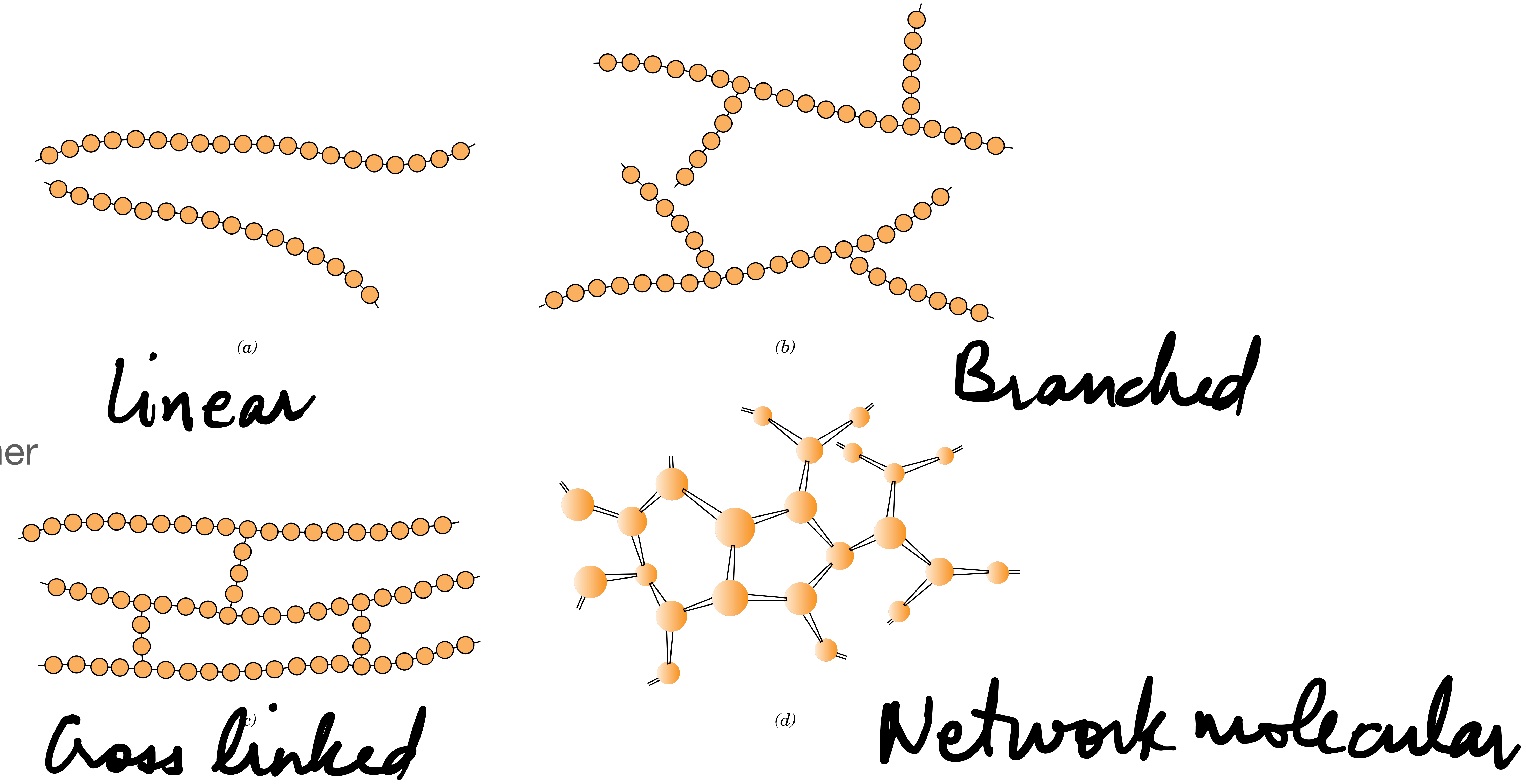
Structure of Polymers: What decides crystallinity in polymers?

Branching





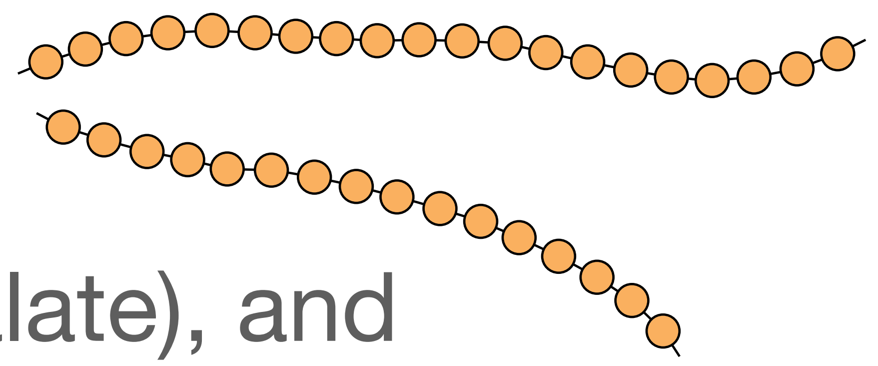
More branching, crosslinking- lesser is the density of polymer

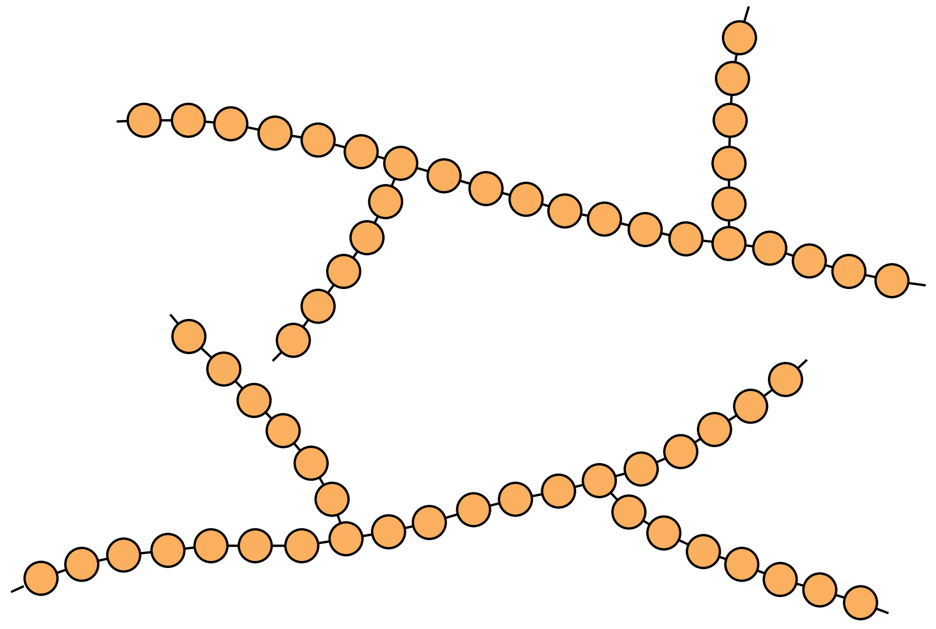
Thermoplasts and Thermosets

Classification based on response to temperature

Thermoplasts:

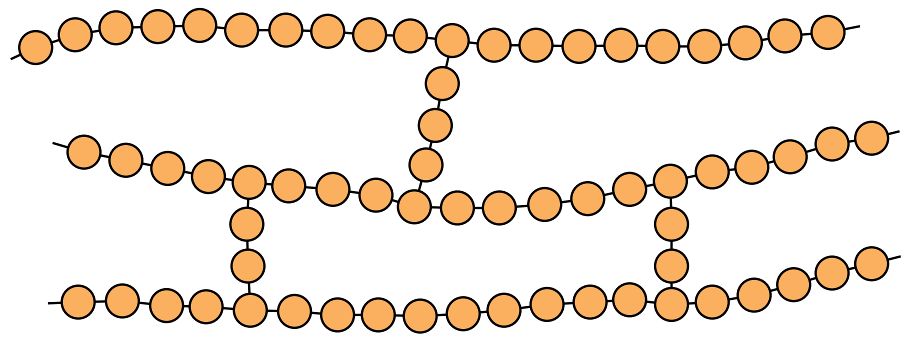
- soften when heated (and eventually liquefy) and harden when cooled—processes that are totally reversible and may be repeated.
- Secondary forces: van der Waals interactions between chains
- Linear and branched polymers
- Examples: polyethylene, polystyrene, poly(ethylene tere- phthalate), and poly(vinyl chloride)

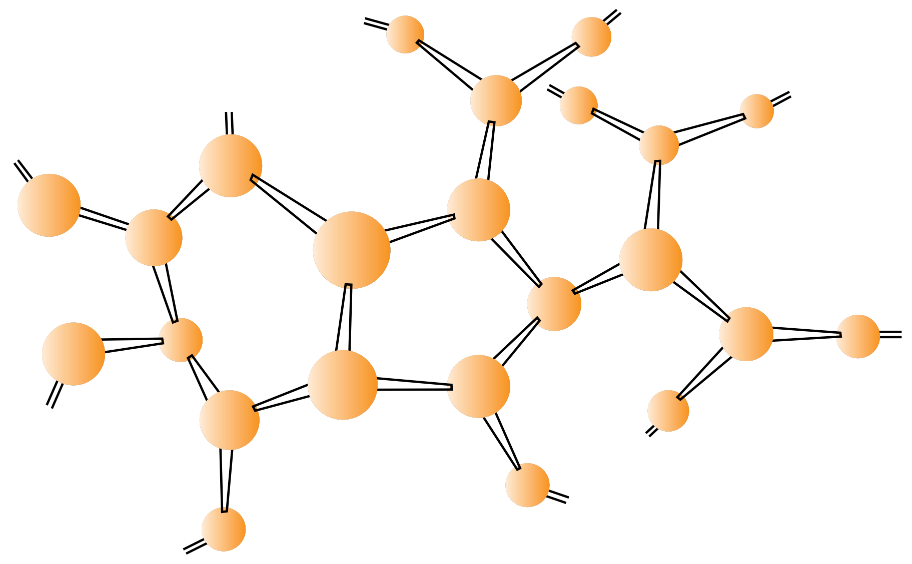




Thermosets:

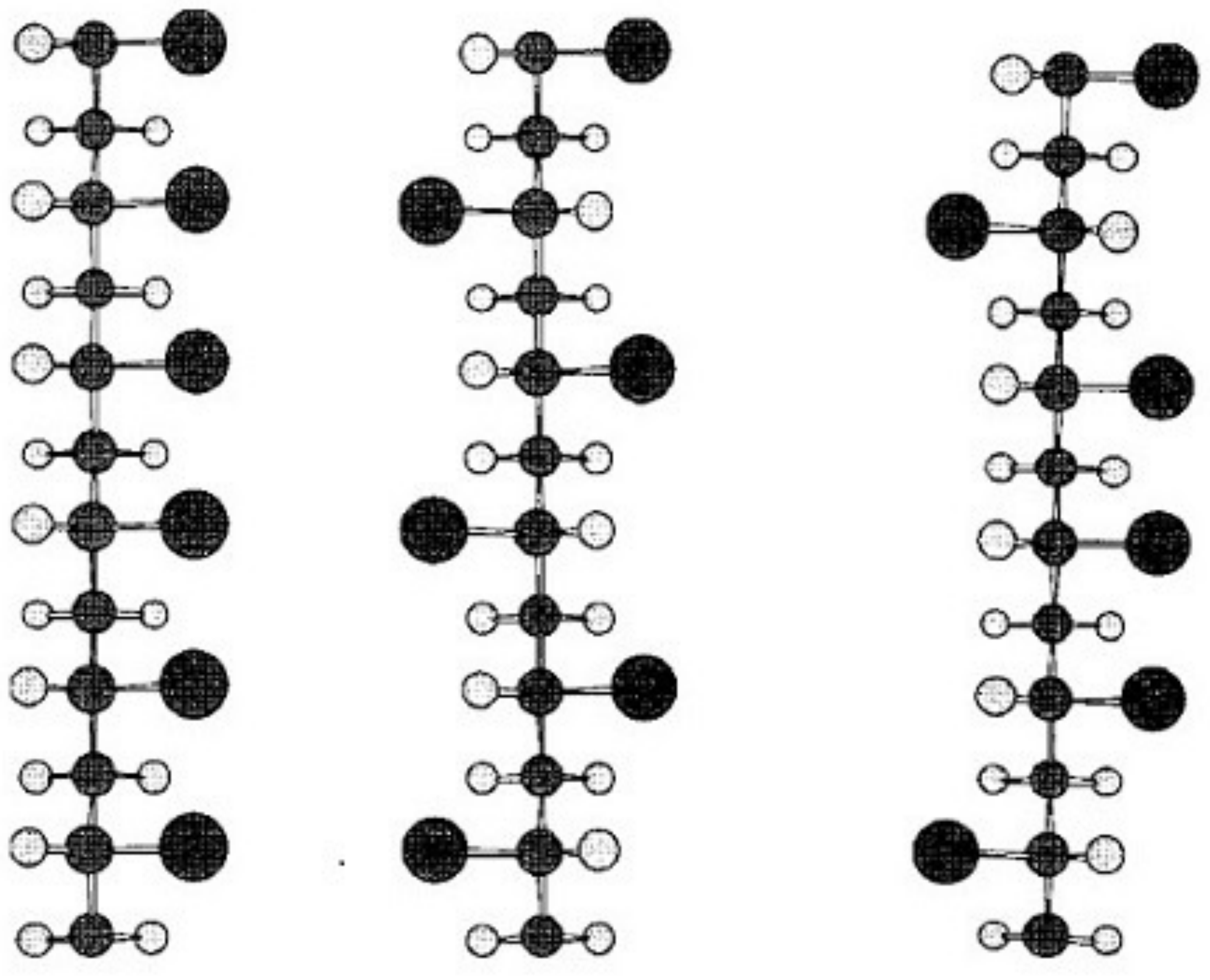
- They become permanently hard during their formation, and do not soften upon heating
- Network polymers and covalent cross linked polymers
- Thermoset polymers are generally harder and stronger than thermoplastics and have better dimensional stability.
- Examples: vulcanized rubbers, epoxies, and phenolics and some polyester resins



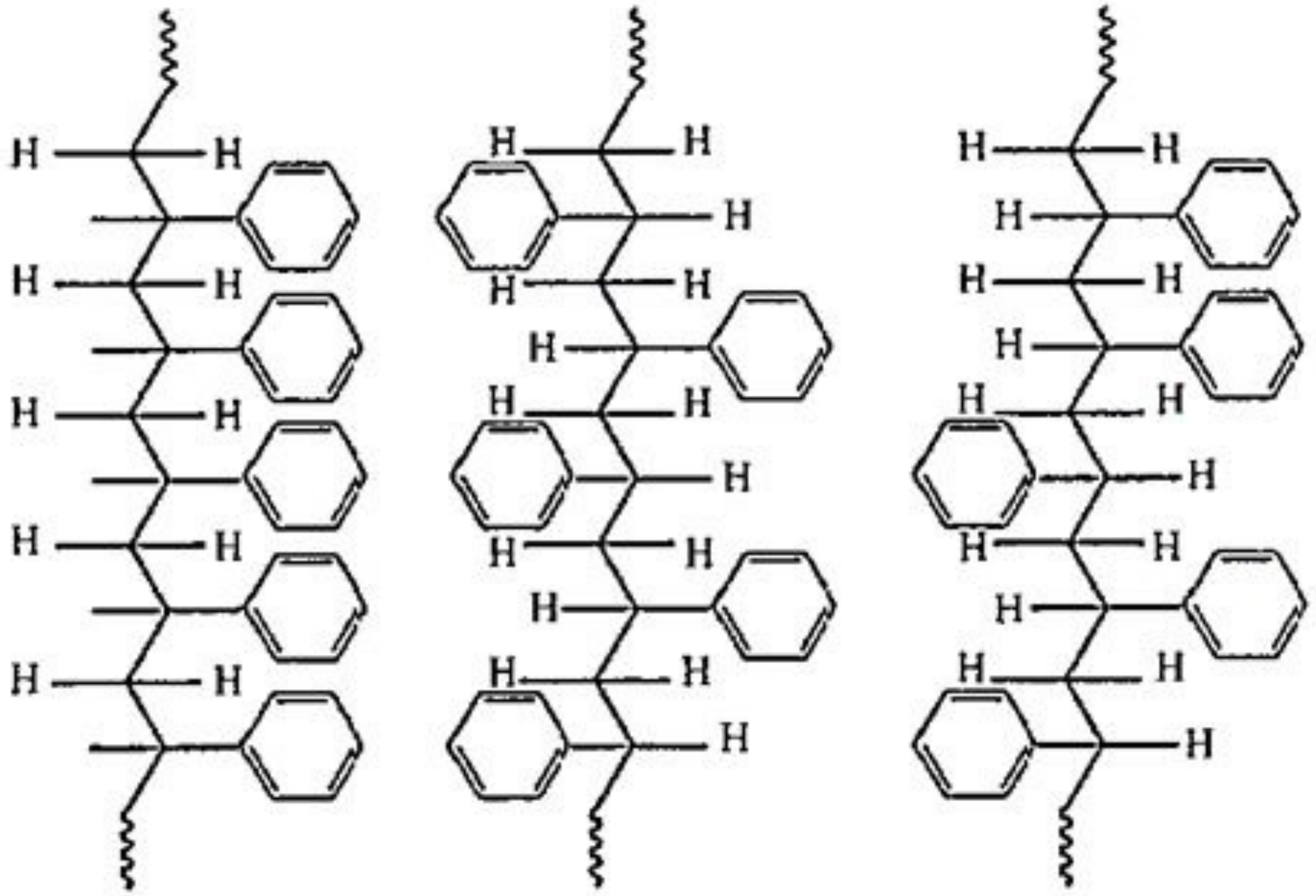


Structure of Polymers: What decides crystallinity in polymers?

Tacticity (Stereochemistry: arrangement or order)



Isotactic Syndiotactic Atactic



Isotactic Syndiotactic Atactic

Isotactic and Syndiotactic can pack easily and density will be higher