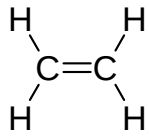
Chapter 14 Polymer structures

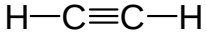
- Hydrocarbon molecules
- Polymer molecules
- Molecular structures & configurations
- Copolymers
- Polymer crystallinity

Hydrocarbon molecules

- Hydrocarbon: composed of hydrogen and carbon
- Single, double, and triple bonds
  - Double bond – ethylene or ethene - C_nH_{2n}



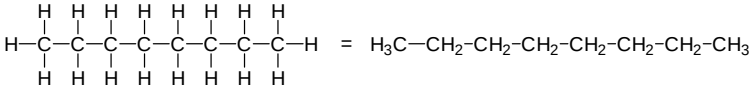
  - 4-bonds, but only 3 atoms bound to C's
  - Triple bond – acetylene or ethyne - C_nH_{2n-2}



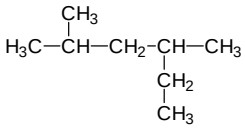
Isomerism

- Isomerism: same composition and different atomic arrangements

N-octane

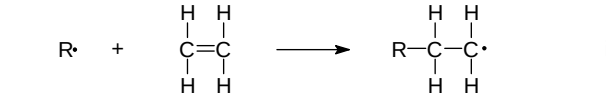


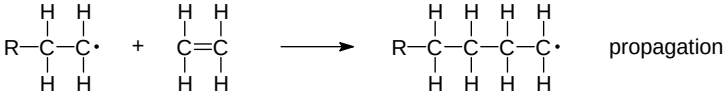
2-methyl-4-ethyl pentane (isooctane)



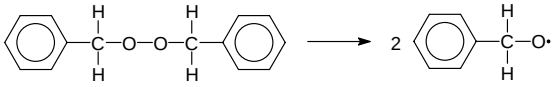
Chemistry of polymers

- Free radical polymerization





- Initiator: example - benzoyl peroxide



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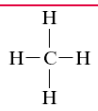
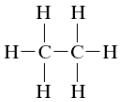
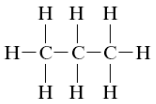
Hydrocarbon molecules

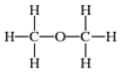
- Bonding
- Boiling T

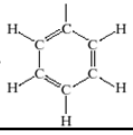
Table 15.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}

Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4		−164
Ethane	C_2H_6		−88.6
Propane	C_3H_8		−42.1
Butane	C_4H_{10}	·	−0.5
Pentane	C_5H_{12}	·	36.1
Hexane	C_6H_{14}	·	69.0

Some common hydrocarbon groups

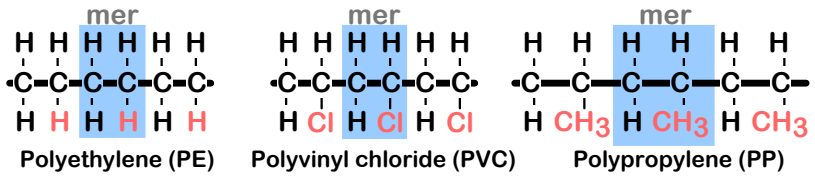
- R and R' represent organic radicals

Family	*Characteristic Unit*	*Representative Compound*	
Alcohols	R—OH		Methyl alcohol
Ethers	R—O—R'		Dimethyl ether
Acids			Acetic acid
Aldehydes			Formaldehyde
Aromatic hydrocarbons			Phenol

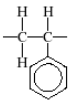
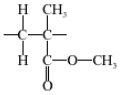
[a] The simplified structure  denotes a phenyl group, 

Polymer molecules

- Macromolecules: molecules with very large size
- mer: structural entities
- monomer: single mer
- polymer: many mers



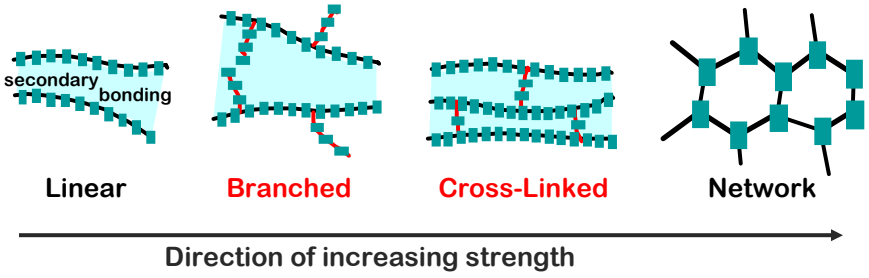
A listing of mer structure of the common polymer materials

Polymer	Repeating (Mer) Structure
Polyethylene (PE)	
Polyvinyl chloride (PVC)	
Polytetrafluoroethylene (PTFE)	
Polypropylene (PP)	
Polystyrene (PS)	
Polymethyl methacrylate (PMMA)	

Polymer structure

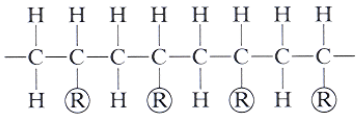
☐ Molecular structure

- **Covalent chain configurations and strength:**

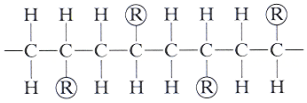


Molecular configuration

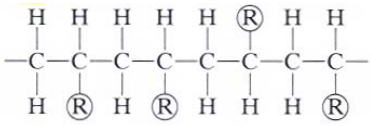
☐ Stereoisomerism: same atomic order and different spatial arrangement



isotactic



syndiotactic

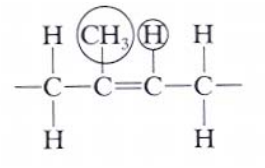


atactic

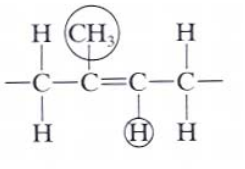
Molecule configuration (continue)

- Geometrical isomerism

Cis



Trans

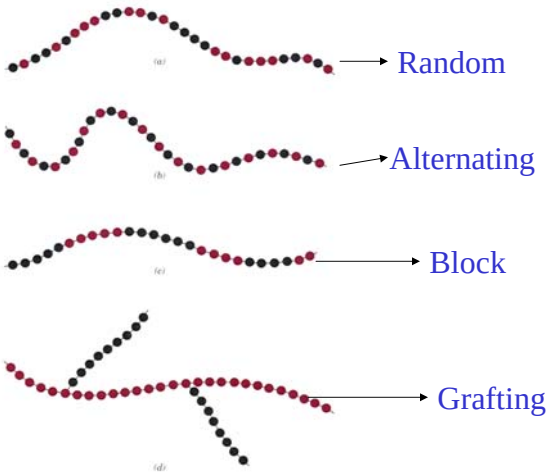


Thermoplastic and thermosetting polymers

- Thermoplastics
  - soften when heated and harden when cooled
  - little crosslink
  - ductile
  - Polyethylene, polypropylene, polycarbonate, polystyrene
- Thermosetting polymers:
  - permanently hard when heat is applied and do not soften upon heating
  - large crosslink (10 to 50% of mers)
  - hard and brittle
  - vulcanized rubber, epoxies, polyester resin, phenolic resin

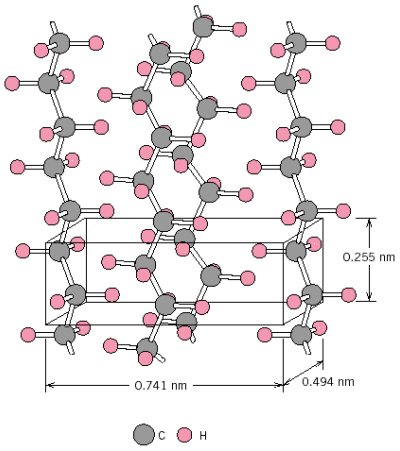
Copolymers

- Homopolymer: same type of mer units along a chain
- Copolymers: two or more different mer units
- Copolymers have four types



Polymer crystallinity

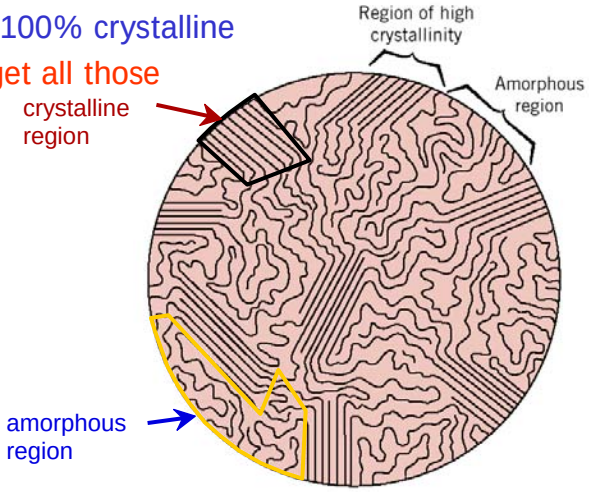
- Crystallinity: the packing of molecular chains to produce an ordered atomic array
- The effects on the degree of polymer crystallinity
  - cooling rate
  - molecule chemistry
  - chain configuration



Arrangement of molecular chains in a unit cell for polyethylene

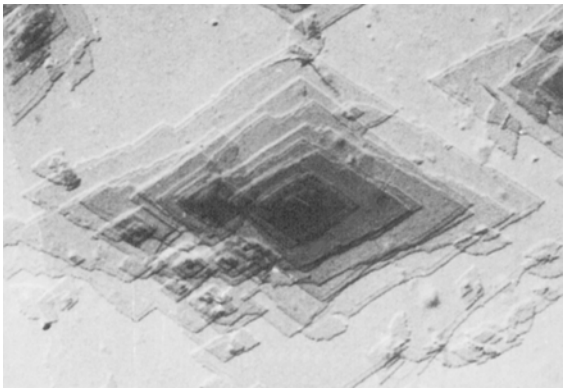
Polymer crystallinity

- Polymers rarely 100% crystalline
  - Too difficult to get all those chains aligned

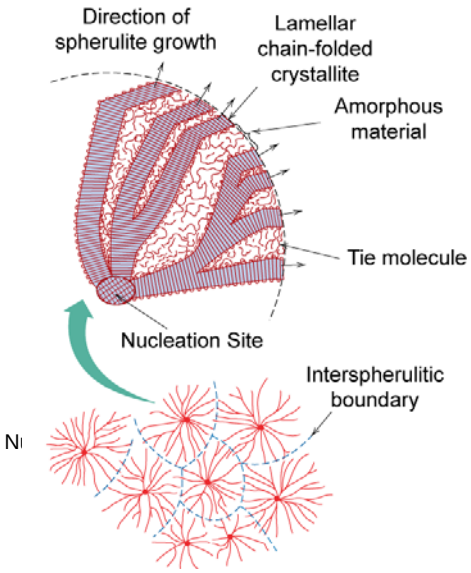


Polymer crystal forms

- Single crystals – only if slow careful growth



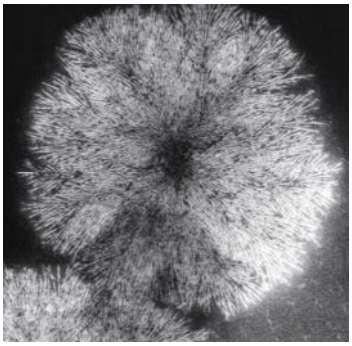
Polymer crystal forms

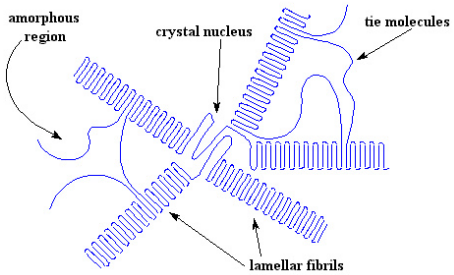


Spherulites – fast growth – forms lamellar (layered) structures

Polymer crystals

- Many semicrystalline polymers are made of spherulitic structure





a polymer crystalline spherulite