# POLYMER STRUCTURES

- What are the general structural and chemical characteristics of polymer molecules?

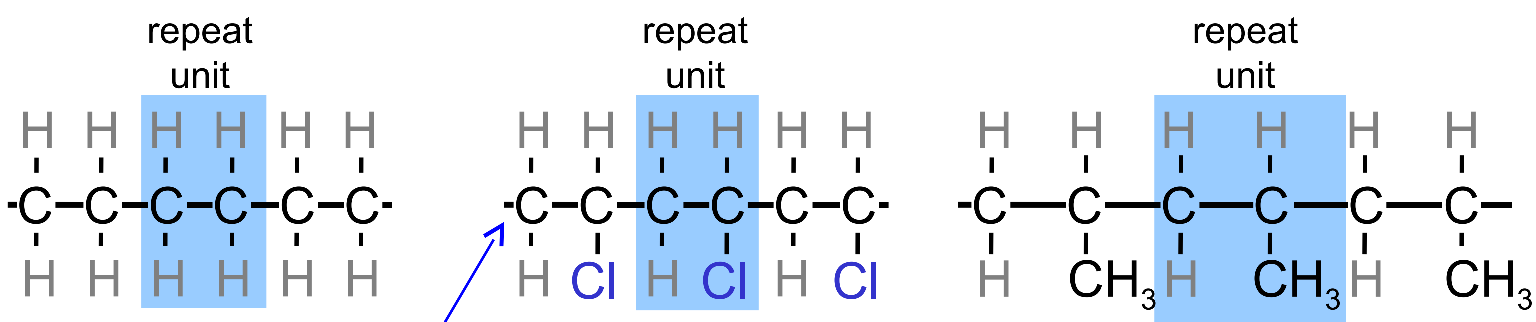
- What are some of the common polymeric materials, and how do they differ chemically?

- How is the crystalline state in polymers different from that in metals and ceramics ?

# Polymer

Poly — mer

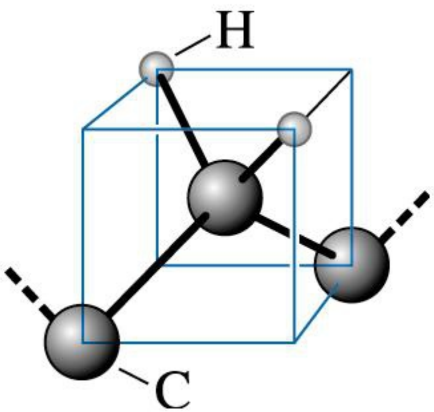
many — repeat unit (building blocks)



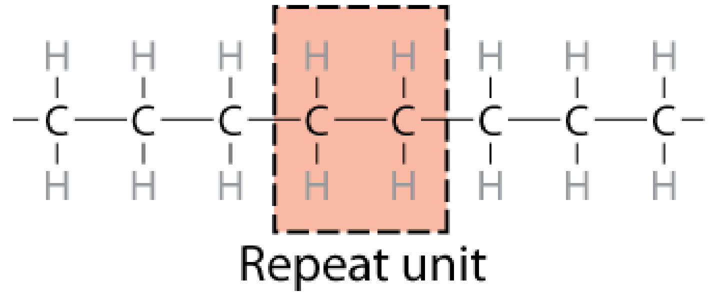

Polyethylene (PE) Poly(vinyl chloride) (PVC) Polypropylene (PP)

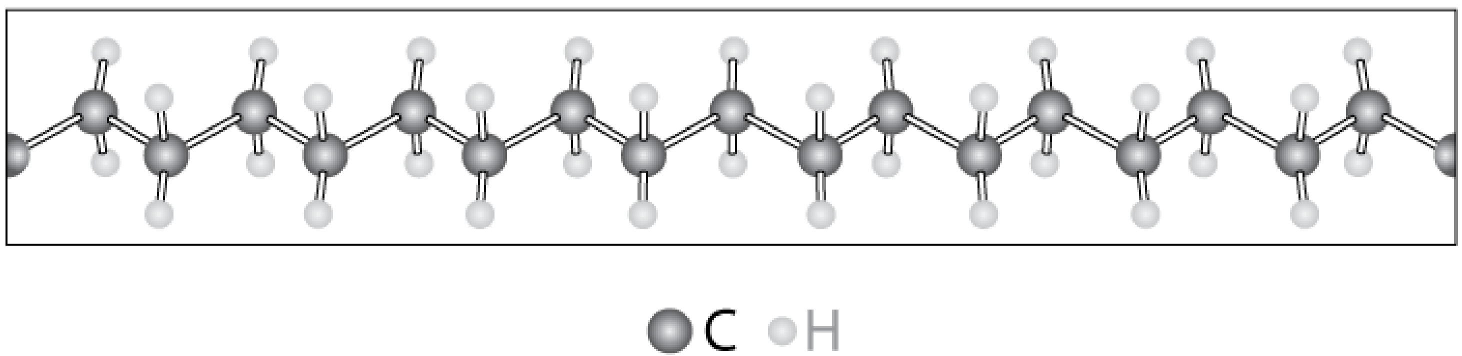
Carbon chain backbone

# Chemistry and Structure of Polyethylene




Tetrahedral arrangement of C-H

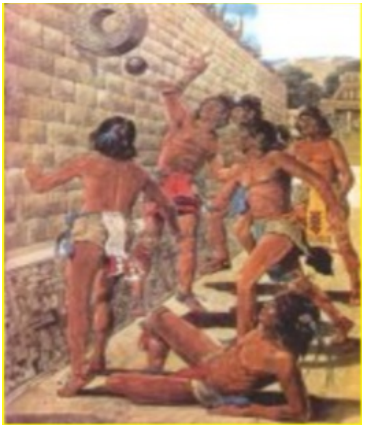



- Polyethylene is a long-chain hydrocarbon.
- Top figure shows repeat unit and chain structures.
- Other figure shows zigzag backbone structure.

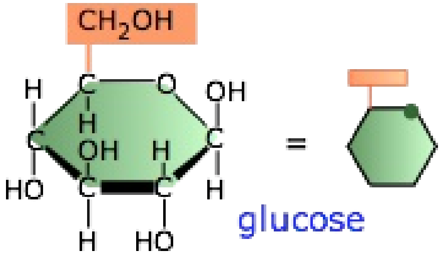
# Ancient Polymers

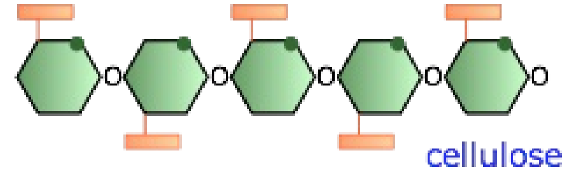
- Naturally occurring polymers (those derived from plants and animals) have been used for centuries.
  - Wood
  - Cotton
  - Leather
  - Rubber
  - Wool
  - Silk



- Oldest known uses
  - Rubber balls used by Incas

# Cellulose

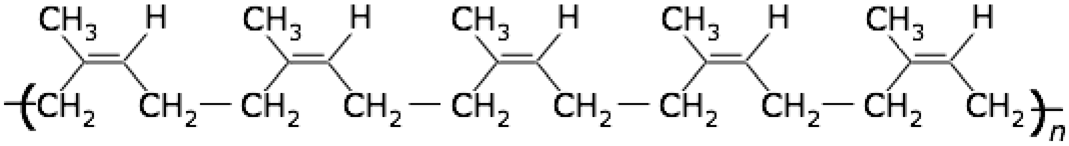



- Cellulose is a highly abundant organic compound. Extensive hydrogen bonding between the chains causes native celluose to be roughly 70% crystalline. It also raises the melting point (>280°C) to above its combustion temperature.
- Cellulose serves as the principal structural component of green plants and wood.
- Cotton is one of the purest forms of cellulose and has been cultivated since ancient times.
- Cotton also serves (along with treated wood pulp) as the source the industrial production of cellulose-derived materials which were the first "plastic" materials of commercial importance.

# Rubber

- A variety of plants produce a sap consisting of a colloidal dispersion of *cis*-polyisoprene. This milky fluid is especially abundant in the rubber tree (*Hevea*); it drips when the bark is wounded.
- After collection, the latex is coagulated to obtain the solid rubber. Natural rubber is thermoplastic, with a glass transition temperature of –70°C.
- Raw natural rubber tends to be sticky when warm and brittle when cold, so it was little more than a novelty material when first introduced in Europe around 1770.
- It did not become generally useful until the mid-nineteenth century when Charles Goodyear found that heating it with sulfur — a process he called *vulcanization* — could greatly improve its properties.



cis-polyisoprene


Opening Remarks

**Evolution of POLYMER (1960-2009)**
*Ian M. Ward, University of Leeds, UK*

**DYNAMERS: Dynamic Molecular and Supramolecular Polymers**
*Jean Marie Lehn , Université Louis Pasteur, Strasbourg, France, Nobel Laureate*

**Supramolecular Assemblies of Smart Block Copolymers as Nanocarriers for Gene and Drug Delivery**
*Kazunori Kataoka , University of Tokyo, Japan*

Coffee Break and Poster Session 1

**Carbon Polymers as CO 2 -negative products**
*Markus Antonietti , Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Potsdam, Germany*

Welcome Reception

## JUNE 2009

**The Future is Black: Graphene and Carbon Materials**
*Klaus Müllen , Max-Planck-Institut für Polymerforschung, Mainz, Germany*

**Designing functional macromolecules : from energy conversion to therapeutics**
*Jean M.J. Fréchet , University of California, Berkeley, USA*

Coffee Break and Poster Session 2

**High Flux Membranes: Properties of Thin Glassy Polymer Films**
*Donald R. Paul , University of Texas, Austin, USA*

Lunch

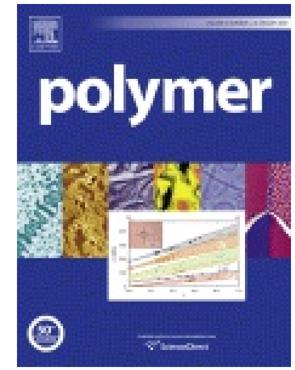
**Hybrid Materials at the Interface between Inorganic and Organic Polymers**
*Clément Sanchez , Université de Paris VI, France*

**Capillary and Cascading Wrinkles**
*Thomas P. Russell , University of Massachusetts, A*

Coffee Break

**ATRP: from mechanism to materials**
*Kris Matyjaszewski , Carnegie Mellon University, P*

Poster Session 3 and Reception




The International Journal for the Science and Technology of Polymers

**Low Cost "Plastic" Solar Cells: Self-Assembly of Bulk Heterojunction Nano-Materials by Spontaneous Phase Separation**
*Alan J. Heeger , University of California, Santa Barbara, USA, Nobel Laureate*

**How Polymer Chains Crystallize: Shifting Paradigms**
*Murugappan Muthukumar, University of Massachusetts, Amherst, USA*

Coffee Break and Poster Session 4

**Periodic Polymers for PhoXonics**
*Edwin L. Thomas , Massachusetts Institute of Technology, USA*

Lunch

**Title TBA**
*Sir Richard Friend , Cambridge University, UK*

**Oleo-chemistry meets supramolecular chemistry: from self-healing plastics to rubbers**
*Ludwik Leibler , ESPCI (Ecole Supérieure de Physique et de Chimie Industrielles), Paris, France*

Coffee Break and Poster Session 5

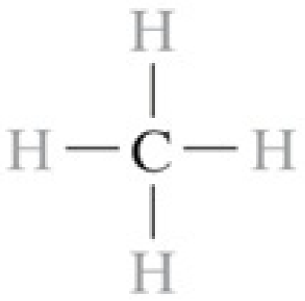
**Reinterpreting the Genetic Code**
*David Tirrell , California Institute of Technology, USA*

Closing Remarks

**End of symposium**

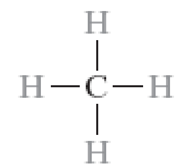
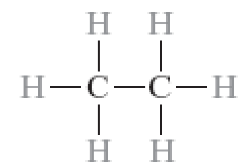
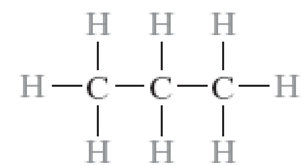
# Hydrocarbon Molecules

- Many organic materials are hydrocarbons (composed of hydrogen and carbon).
- Most polymers are made up of H and C.
- The bonds between the hydrocarbon molecules are covalent.
- Each carbon atom has 4 electrons that may be covalently bonded, the hydrogen atom has 1 electron for bonding.
- A single covalent bond exists when each of the 2 bonding atoms contributes one electron (ex: methane, $CH_4$).



# Saturated Hydrocarbons

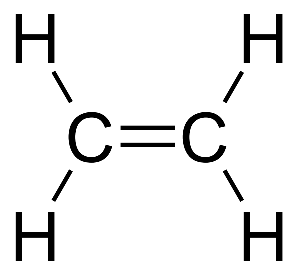
- Each carbon has a single bond to 4 other atoms; the 4 valence electrons are bonded, the molecule is stable. Examples are seen in the table.
- The covalent bonds in each molecule are strong, but only weak hydrogen and van der Waals bonds exist between the molecules.

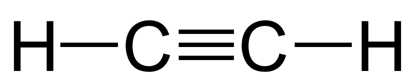
| *Name* | *Composition* | *Structure* | *Boiling Point (°C)* |
|---|---|---|---|
| Methane | $CH_4$ |  | −164 |
| Ethane | $C_2H_6$ |  | −88.6 |
| Propane | $C_3H_8$ |  | −42.1 |
| Butane | $C_4H_{10}$ | | −0.5 |
| Pentane | $C_5H_{12}$ | | 36.1 |
| Hexane | $C_6H_{14}$ | | 69.0 |

- Most of these hydrocarbons have relatively low melting and boiling points.
- However, boiling temperatures rise with increasing molecular weight.

# Unsaturated Hydrocarbons

- Double & triple bonds are somewhat unstable – involve sharing 2 or 3 pairs of electrons, respectively. They can also form new bonds
  - Double bond found in ethylene - $C_2H_4$





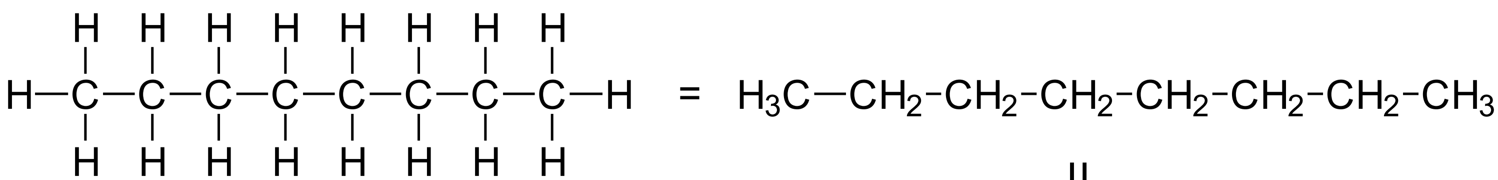
  - Triple bond found in acetylene - $C_2H_2$

# Isomerism

- Two compounds with same chemical formula can have different structures (atomic arrangements).

for example: $C_8H_{18}$

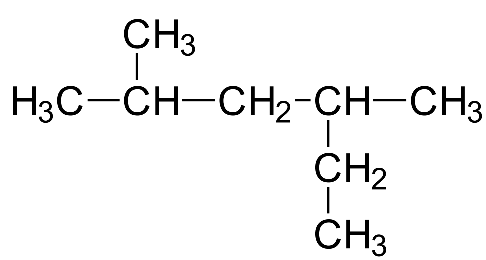
- normal-octane



$$\Downarrow$$

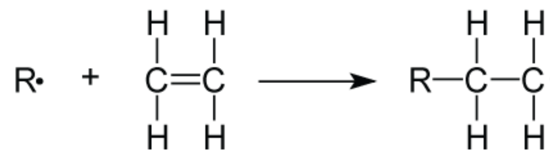
$$H_3C{-}(CH_2)_6{-}CH_3$$

- 2,4-dimethylhexane

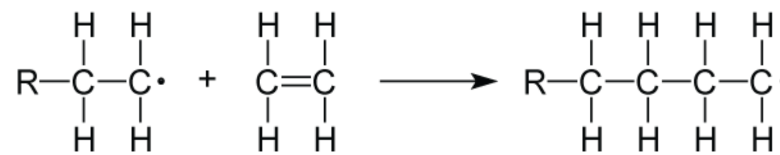


# Addition (Chain) Polymerization

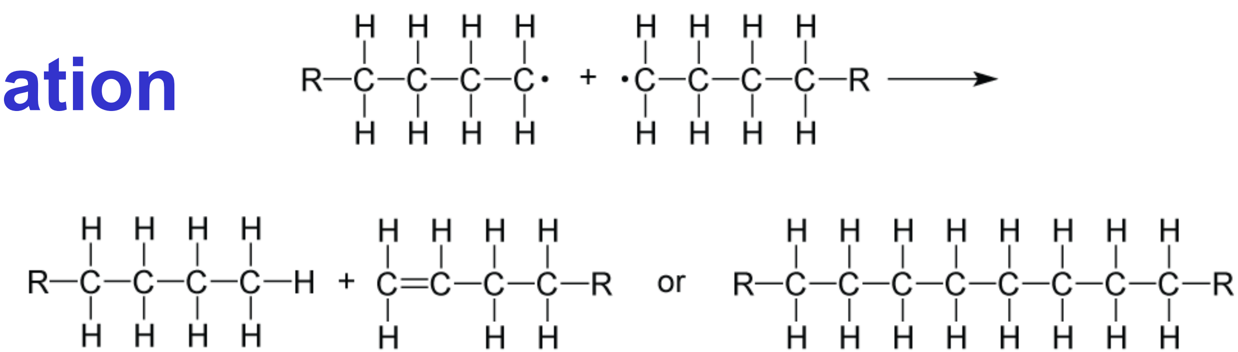
– **Initiation**



– **Propagation**



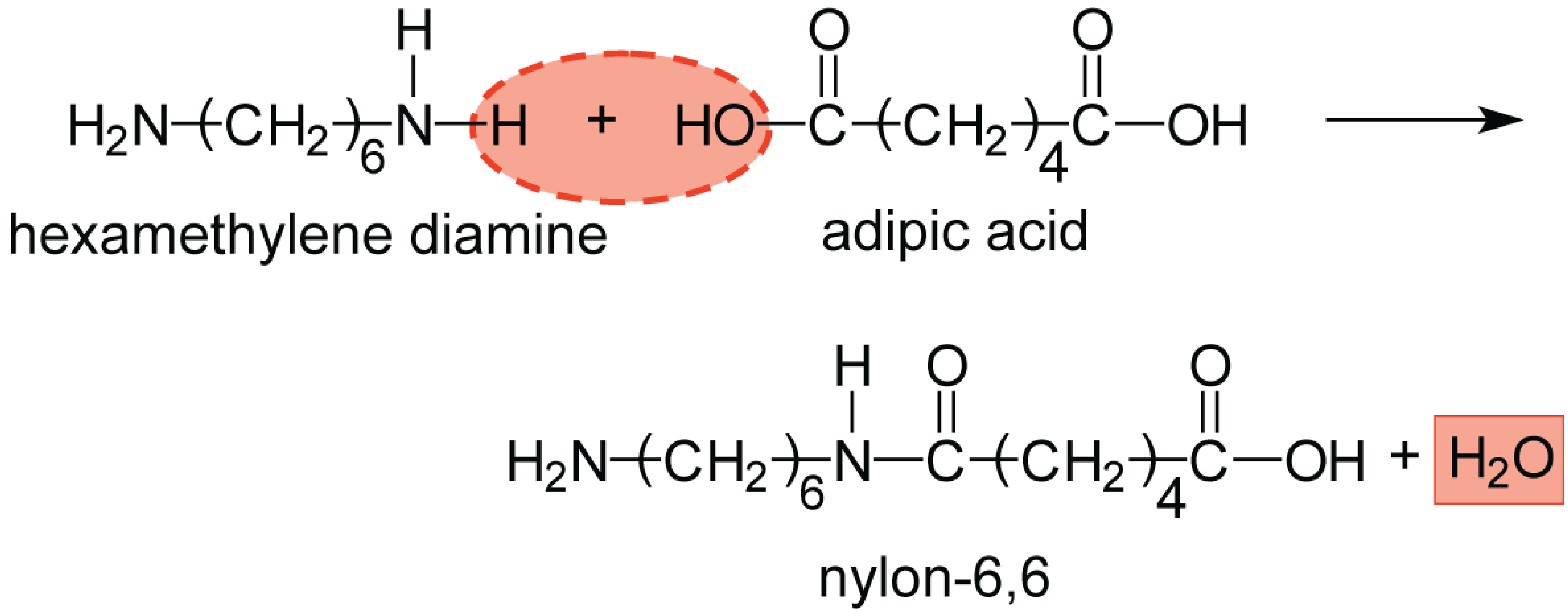
– **Termination**



Disproportionation

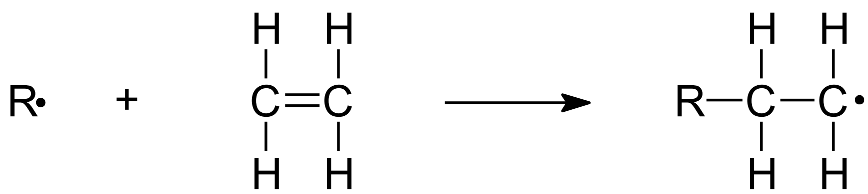
Combination

# Condensation (Step) Polymerization



# Polymerization

- Free radical polymerization: ethylene gas reacts with the initiator (catalyst). ("R." is the unpaired electron)

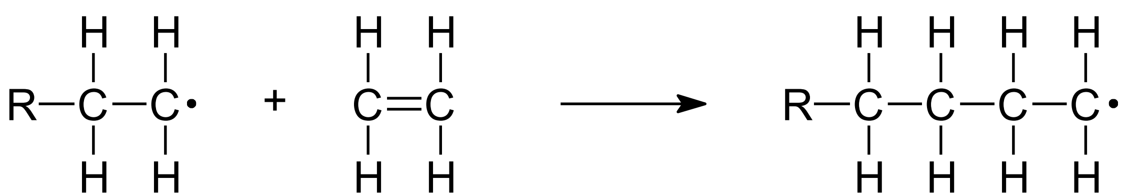


initiation

free radical

monomer (ethylene)

Monomer refers to the small molecule from which a polymer is synthesized.



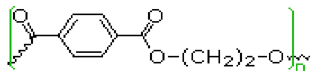
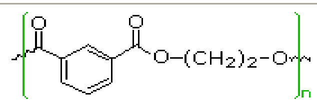
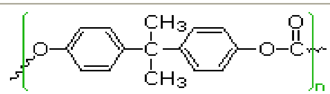
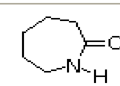
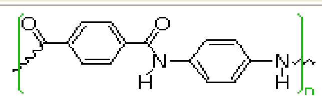
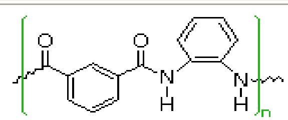
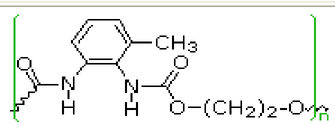
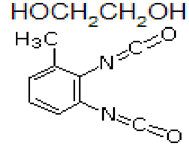
propagation

dimer

# Some Common Addition Polymers

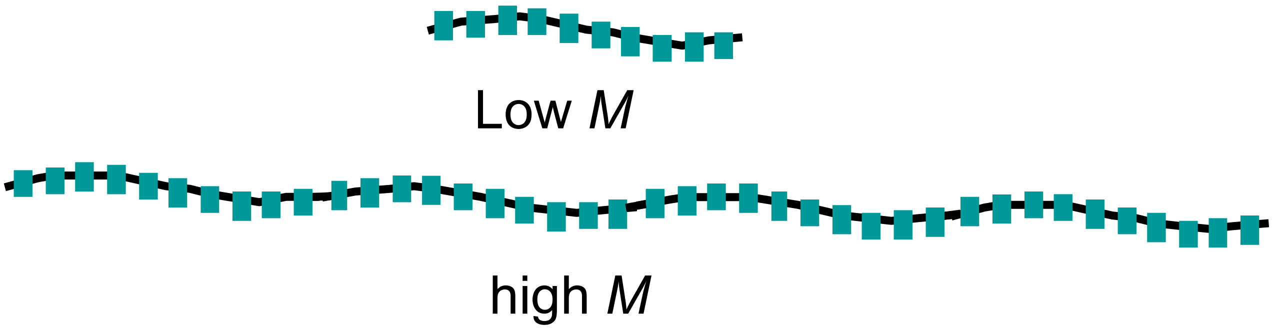
| Name(s) | Formula | Monomer | Properties | Uses |
|---|---|---|---|---|
| **Polyethylene** low density (LDPE) | $–(CH_2\text{-}CH_2)_n–$ | ethylene $CH_2{=}CH_2$ | soft, waxy solid | film wrap, plastic bags |
| **Polyethylene** high density (HDPE) | $–(CH_2\text{-}CH_2)_n–$ | ethylene $CH_2{=}CH_2$ | rigid, translucent solid | electrical insulation bottles, toys |
| **Polypropylene** (PP) different grades | $–[CH_2\text{-}CH(CH_3)]_n–$ | propylene $CH_2{=}CHCH_3$ | atactic: soft, elastic solid isotactic: hard, strong solid | similar to LDPE carpet, upholstery |
| **Poly(vinyl chloride)** (PVC) | $–(CH_2\text{-}CHCl)_n–$ | vinyl chloride $CH_2{=}CHCl$ | strong rigid solid | pipes, siding, flooring |
| **Poly(vinylidene chloride)** (Saran A) | $–(CH_2\text{-}CCl_2)_n–$ | vinylidene chloride $CH_2{=}CCl_2$ | dense, high-melting solid | seat covers, films |
| **Polystyrene** (PS) | $–[CH_2\text{-}CH(C_6H_5)]_n–$ | styrene $CH_2{=}CHC_6H_5$ | hard, rigid, clear solid soluble in organic solvents | toys, cabinets packaging (foamed) |
| **Polyacrylonitrile** (PAN, Orlon, Acrilan) | $–(CH_2\text{-}CHCN)_n–$ | acrylonitrile $CH_2{=}CHCN$ | high-melting solid soluble in organic solvents | rugs, blankets clothing |
| **Polytetrafluoroethylene** (PTFE, Teflon) | $–(CF_2\text{-}CF_2)_n–$ | tetrafluoroethylene $CF_2{=}CF_2$ | resistant, smooth solid | non-stick surfaces electrical insulation |
| **Poly(methyl methacrylate)** (PMMA, Lucite, Plexiglas) | $–[CH_2\text{-}C(CH_3)CO_2CH_3]_n–$ | methyl methacrylate $CH_2{=}C(CH_3)CO_2CH_3$ | hard, transparent solid | lighting covers, signs skylights |
| **Poly(vinyl acetate)** (PVAc) | $–(CH_2\text{-}CHOCOCH_3)_n–$ | vinyl acetate $CH_2{=}CHOCOCH_3$ | soft, sticky solid | latex paints, adhesives |
| **cis-Polyisoprene** natural rubber | $–[CH_2\text{-}CH{=}C(CH_3)\text{-}CH_2]_n–$ | isoprene $CH_2{=}CH\text{-}C(CH_3){=}CH_2$ | soft, sticky solid | requires vulcanization for practical use |
| **Polychloroprene** (cis + trans) (Neoprene) | $–[CH_2\text{-}CH{=}CCl\text{-}CH_2]_n–$ | chloroprene $CH_2{=}CH\text{-}CCl{=}CH_2$ | tough, rubbery solid | synthetic rubber oil resistant |

# Some Condensation Polymers

| Formula | Type | Components | $T_g$ °C | $T_m$ °C |
|---|---|---|---|---|
| ~$[CO(CH_2)_4CO\text{-}OCH_2CH_2O]_n$~ | **polyester** | $HO_2C\text{-}(CH_2)_4\text{-}CO_2H$<br>$HO\text{-}CH_2CH_2\text{-}OH$ | < 0 | 50 |
|  | **polyester**<br>Dacron<br>Mylar | para $HO_2C\text{-}C_6H_4\text{-}CO_2H$<br>$HO\text{-}CH_2CH_2\text{-}OH$ | 70 | 265 |
|  | **polyester** | meta $HO_2C\text{-}C_6H_4\text{-}CO_2H$<br>$HO\text{-}CH_2CH_2\text{-}OH$ | 50 | 240 |
|  | **polycarbonate**<br>Lexan | $(HO\text{-}C_6H_4\text{-})_2C(CH_3)_2$<br>(Bisphenol A)<br>$X_2C{=}O$<br>($X = OCH_3$ or Cl) | 150 | 267 |
| ~$[CO(CH_2)_4CO\text{-}NH(CH_2)_6NH]_n$~ | **polyamide**<br>Nylon 66 | $HO_2C\text{-}(CH_2)_4\text{-}CO_2H$<br>$H_2N\text{-}(CH_2)_6\text{-}NH_2$ | 45 | 265 |
| ~$[CO(CH_2)_5NH]_n$~ | **polyamide**<br>Nylon 6<br>Perlon |  | 53 | 223 |
|  | **polyamide**<br>Kevlar | para $HO_2C\text{-}C_6H_4\text{-}CO_2H$<br>para $H_2N\text{-}C_6H_4\text{-}NH_2$ | --- | 500 |
|  | **polyamide**<br>Nomex | meta $HO_2C\text{-}C_6H_4\text{-}CO_2H$<br>meta $H_2N\text{-}C_6H_4\text{-}NH_2$ | 273 | 390 |
|  | **polyurethane**<br>Spandex | $HOCH_2CH_2OH$<br> | 52 | --- |

# MOLECULAR WEIGHT

- Molecular weight, *M*: Mass of a mole of chains.

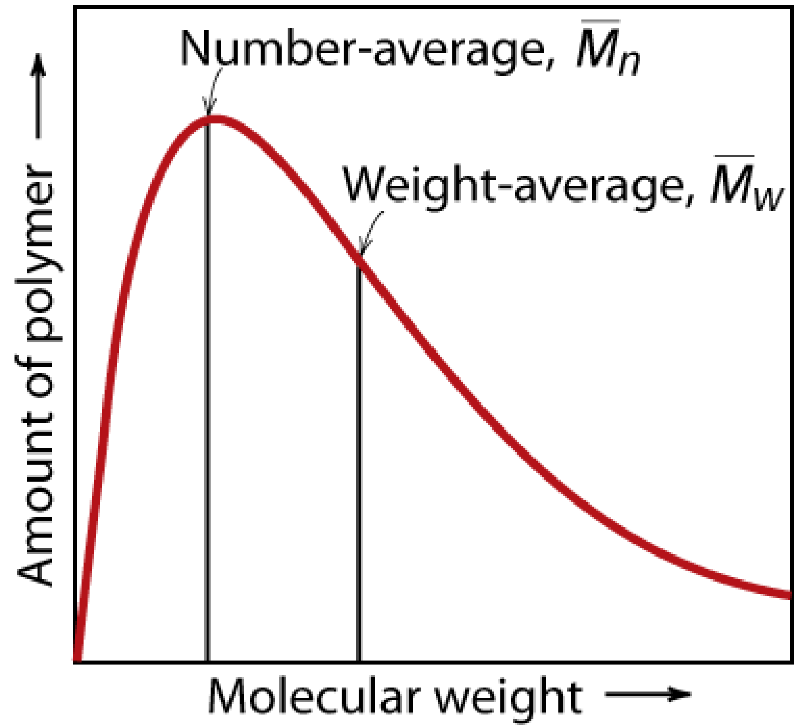



- Polymers can have various lengths depending on the number of repeat units.
- During the polymerization process not all chains in a polymer grow to the same length, so there is a distribution of molecular weights. There are several ways of defining an average molecular weight.
- The molecular weight distribution in a polymer describes the relationship between the number of moles of each polymer species and the molar mass of that species.

# MOLECULAR WEIGHT DISTRIBUTION

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

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




$\overline{M}_n$ = the number average molecular weight (mass)

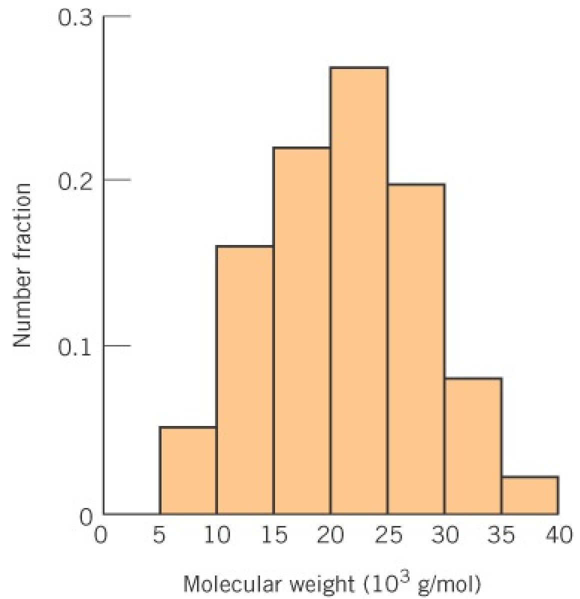
$M_i$ = mean (middle) molecular weight of size range *i*

$x_i$ = number fraction of chains in size range *i*

$w_i$ = weight fraction of chains in size range *i*

**Table 4.4a** **Data Used for Number-Average Molecular Weight Computations in Example Problem 4.1**

| Molecular Weight Range (g/mol) | Mean $M_i$ (g/mol) | $x_i$ | $x_iM_i$ |
|---|---|---|---|
| 5,000–10,000 | 7,500 | 0.05 | 375 |
| 10,000–15,000 | 12,500 | 0.16 | 2000 |
| 15,000–20,000 | 17,500 | 0.22 | 3850 |
| 20,000–25,000 | 22,500 | 0.27 | 6075 |
| 25,000–30,000 | 27,500 | 0.20 | 5500 |
| 30,000–35,000 | 32,500 | 0.08 | 2600 |
| 35,000–40,000 | 37,500 | 0.02 | 750 |
| | | | $\bar{M}_n$ = 21,150 |



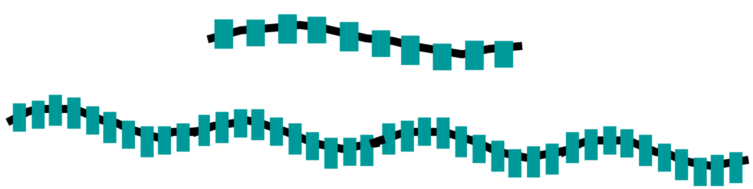
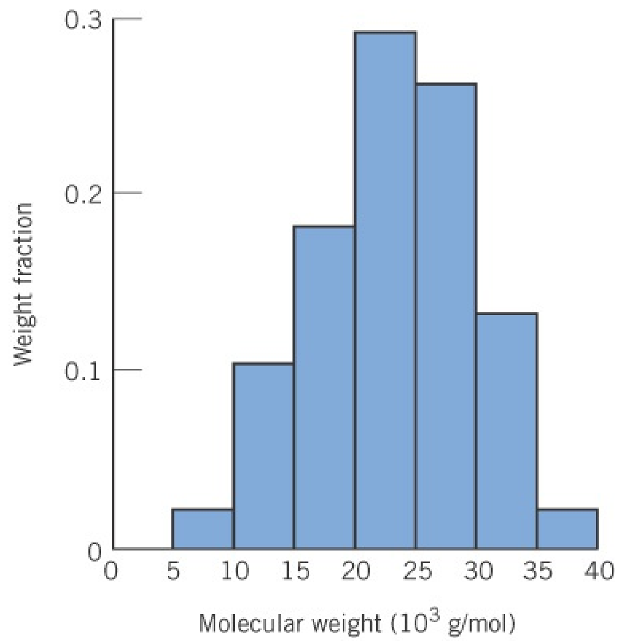



**Table 4.4b Data Used for Weight-Average Molecular Weight Computations in Example Problem 4.1**

| *Molecular Weight Range (g/mol)* | *Mean $M_i$ (g/mol)* | $w_i$ | $w_iM_i$ |
|---|---|---|---|
| 5,000–10,000 | 7,500 | 0.02 | 150 |
| 10,000–15,000 | 12,500 | 0.10 | 1250 |
| 15,000–20,000 | 17,500 | 0.18 | 3150 |
| 20,000–25,000 | 22,500 | 0.29 | 6525 |
| 25,000–30,000 | 27,500 | 0.26 | 7150 |
| 30,000–35,000 | 32,500 | 0.13 | 4225 |
| 35,000–40,000 | 37,500 | 0.02 | 750 |
| | | | $\bar{M}_w = 23{,}200$ |



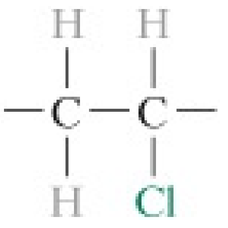
# Degree of Polymerization, *DP*

*DP* = average number of repeat units per chain

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

where $m$ = repeat unit molecular weight

Poly(vinyl chloride) (PVC)



Ex. problem 4.1b,

for PVC: m = 2(carbon) + 3(hydrogen) + 1(Clorine)

(from front of book) = 2(12.011) + 3(1.008) + 1(35.45)

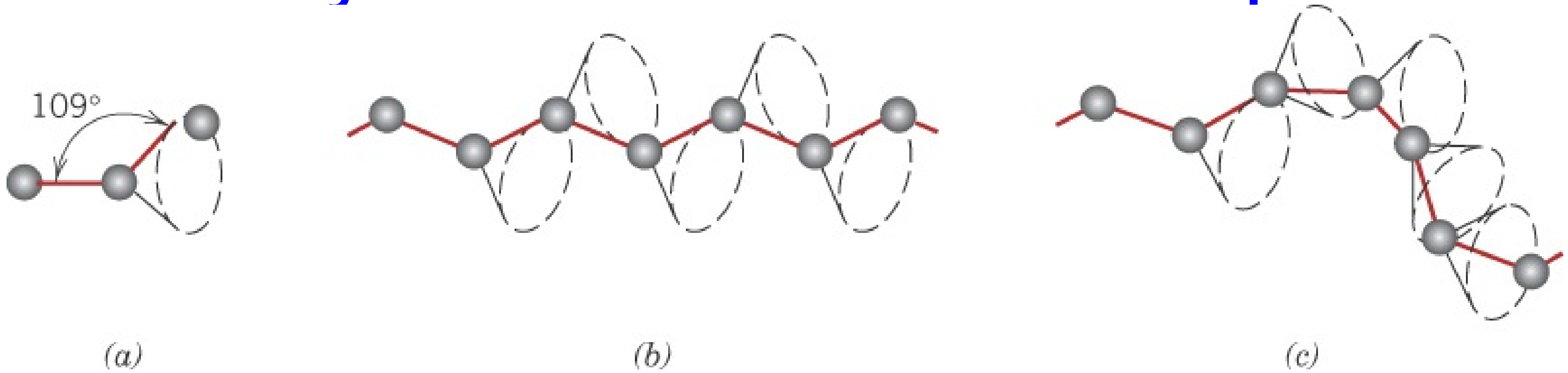
= 62.496 g/mol

DP = 21,150 / 62.496 = 338.42

# Polymer Chain Lengths

- Many polymer properties are affected by the length of the polymer chains. For example, the melting temperature increases with increasing molecular weight.
- At room temp, polymers with very short chains (roughly 100 g/mol) will exist as liquids.
- Those with weights of 1000 g/mol are typically waxy solids and soft resins.
- Solid polymers range between 10,000 and several million g/mol.
- The molecular weight affects the polymer's properties (examples: elastic modulus & strength).

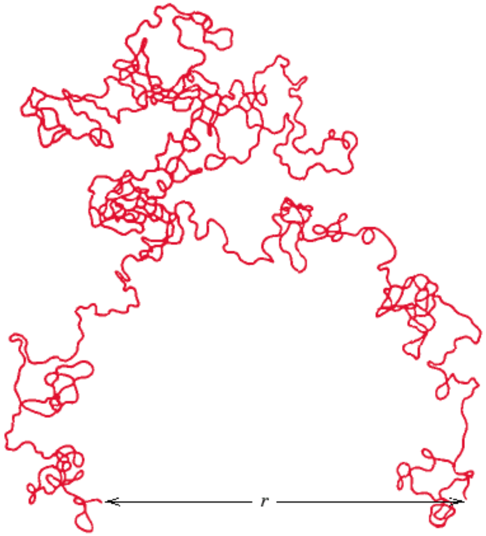
# Polymers – Molecular Shape



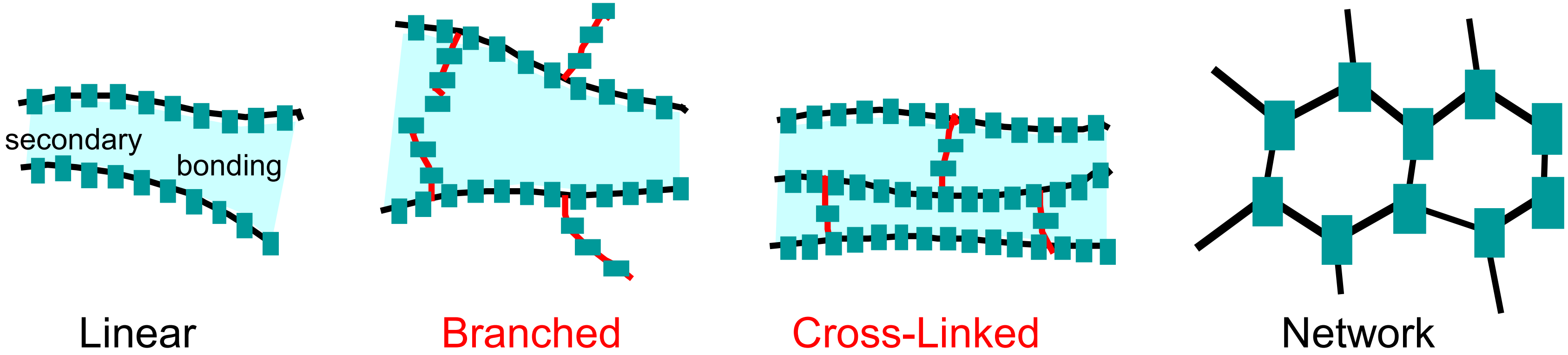

- Straight (b) and twisted (c) chain segments are generated when the backbone carbon atoms (dark circles) are oriented as in the figure above.
- Chain bending and twisting are possible by rotation of carbon atoms around their chain bonds.
- Some of the polymer mechanical and thermal characteristics are a function of the chain segment rotation in response to applied stresses or thermal vibrations.

# Chain End-to-End Distance, *r*

- Representation of a single polymer chain molecule that has numerous random kinks and coils produced by chain bond rotations; it is very similar to a heavily tangled fishing line.
- "r" is the end to end distance of the polymer chain which is much smaller than the total chain length.

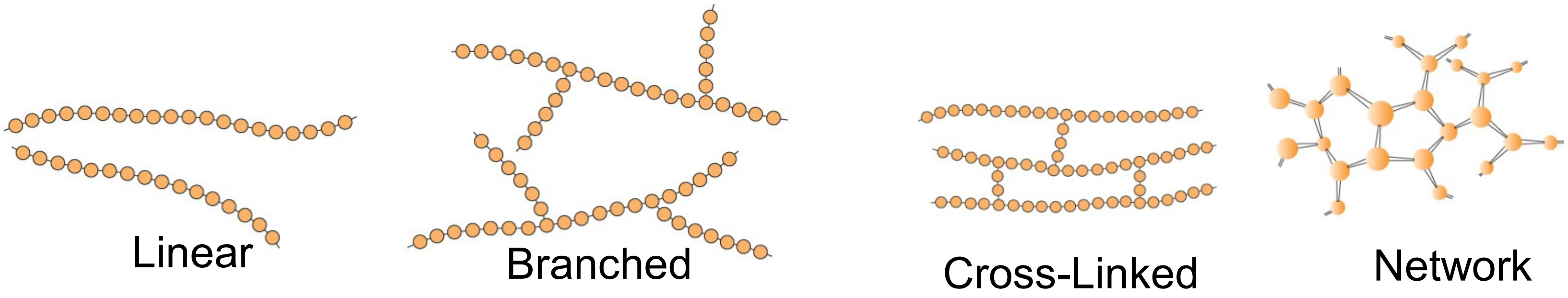


# Molecular Structures for Polymers



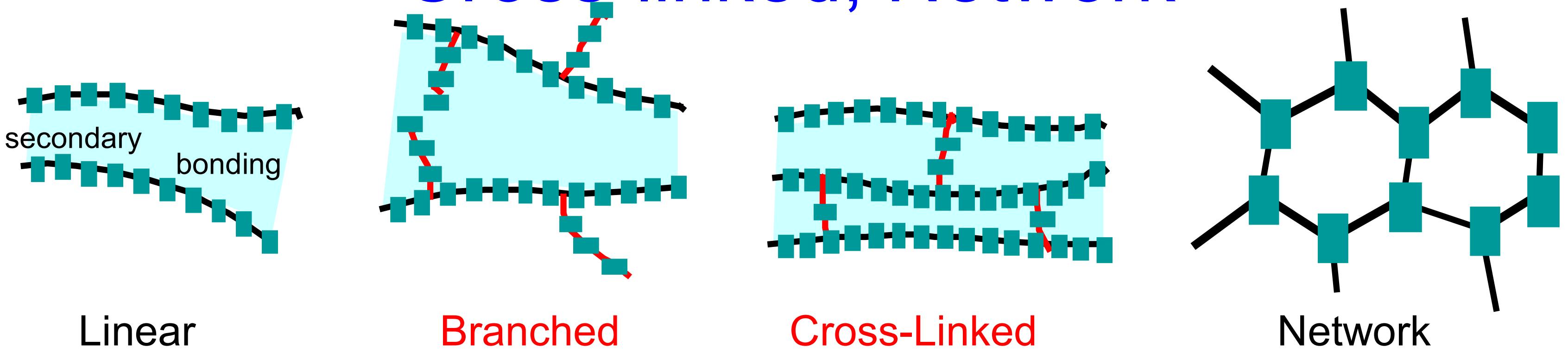

- The physical characteristics of a polymer depend also on differences in the structure of the molecular chains (other variables are shape and weight).
- Linear polymers have repeat units joined end to end in single chains. There may be extensive van der Waals and hydrogen bonding between the chains. Examples: polyethylene, PVC, nylon.

# Molecular Structures- Branched




- Where side-branch chains have connected to main chains, these are termed branched polymers. Linear structures may have side-branching.
- HDPE – high density polyethylene is primarily a linear polymer with minor branching,  while LDPE – low density polyethylene contains numerous short chain branches.
- Greater chain linearity and chain length tend to increase the melting point and improve the physical and mechanical properties of the polymer due to greater crystallinity.

# Molecular Structures – Cross-linked, Network




- In cross-linked polymers, adjacent linear chains are joined to one another at various positions by covalent bonding of atoms. Examples are the rubber elastic materials.
- Small molecules that form 3 or more active covalent bonds create structures called network polymers. Examples are the epoxies and polyurethanes.

# Thermoplastics and Thermosets

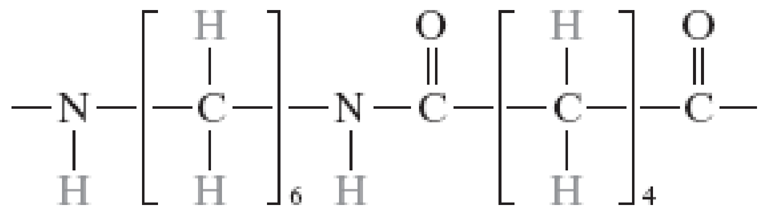
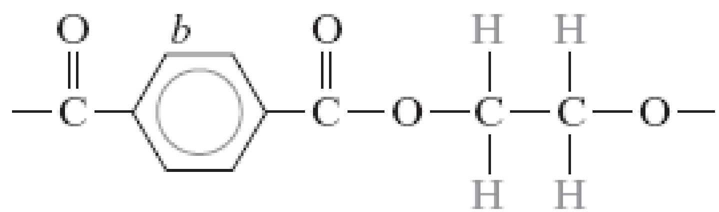
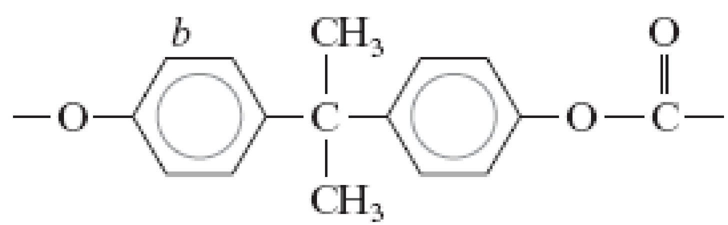
- The response of a polymer to mechanical forces at elevated temperature is related to its dominant molecular structure.
- One classification of polymers is according to its behavior and rising temperature. Thermoplastics and Thermosets are the 2 categories.
- A thermoplastic is a polymer that turns to a liquid when heated and freezes to a very glassy state when cooled sufficiently.
- Most thermoplastics are high-molecular-weight polymers whose chains associate through weak Van der Waals forces (polyethylene); stronger dipole-dipole interactions and hydrogen bonding (nylon).

# Thermoplastics and Thermosets

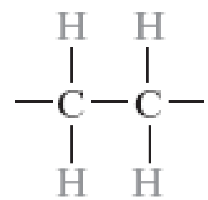
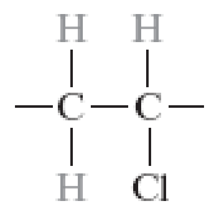
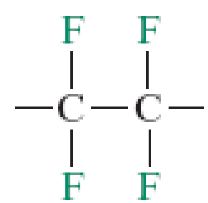
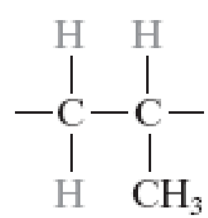
- Thermoplastic polymers differ from thermosetting polymers (Bakelite, vulcanized rubber) since thermoplastics can be remelted and remolded.
- Thermosetting plastics when heated, will chemically decompose, so they can not be recycled. Yet, once a thermoset is cured it tends to be stronger than a thermoplastic.
- Typically, linear polymers with minor branched structures (and flexible chains) are thermoplastics. The networked structures are thermosets.

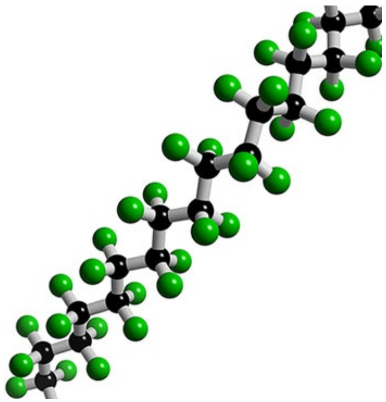
# Examples of Thermoplastics

**Table 4.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials**

| *Polymer* | *Repeat Unit* |
| --- | --- |
| Poly(hexamethylene adipamide) (nylon 6,6) |  |
| Poly(ethylene terephthalate) (PET, a polyester) |  |
| Polycarbonate (PC) |  |

# More Examples of Thermoplastics

| Polymer | Repeat Unit |
| --- | --- |
| Polyethylene (PE) |  |
| Poly(vinyl chloride) (PVC) |  |
| Polytetrafluoroethylene (PTFE) |  |
| Polypropylene (PP) |  |



PTFE

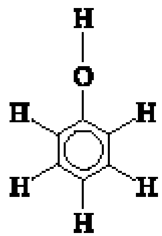
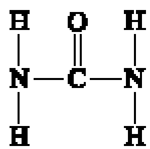
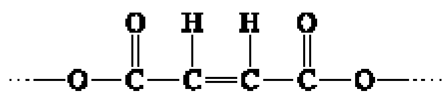
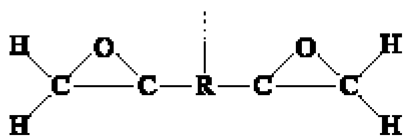
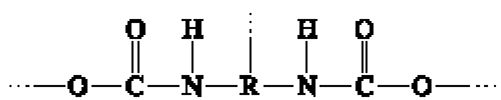
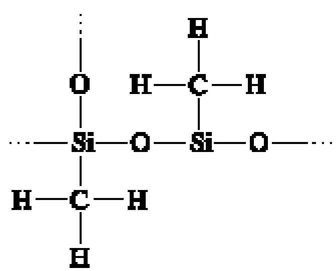
http://www2.dupont.com/Teflon/en_US/index.html

http://en.wikipedia.org/wiki/Teflon

# Specific Thermoplastic Properties

| | 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 |

# Thermoset data

| 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 |

# Thermoset Properties

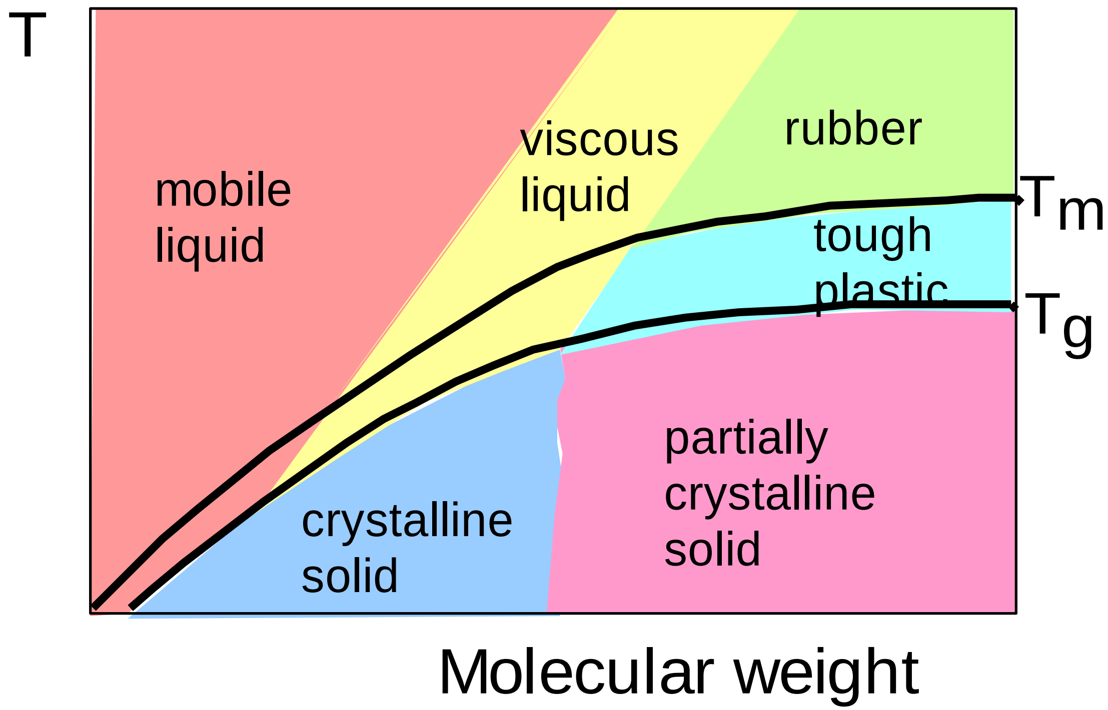
| | Tensile Strength (psi) | % Elongation | Elastic Modulus (psi) | Density ($g/cm^3$) |
|---|---|---|---|---|
| Phenolics | 9,000 | 2 | 1300 | 1.27 |
| Amines | 10,000 | 1 | 1600 | 1.50 |
| Polyesters | 13,000 | 3 | 650 | 1.28 |
| Epoxies | 15,000 | 6 | 500 | 1.25 |
| Urethanes | 10,000 | 6 | | 1.30 |
| Silicone | 4,000 | 0 | 1200 | 1.55 |

# Specific Elastomeric Properties

Elastomers, often referred to as rubber, can be a thermoplastic or a thermoset depending on the structure. They are excellent for parts requiring flexiblity, 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 |

# Thermoplastic vs Thermoset




- Thermoplastics:
  --little cross linking
  --ductile
  --soften with heating
  --polyethylene
  polypropylene
  polycarbonate
  polystyrene

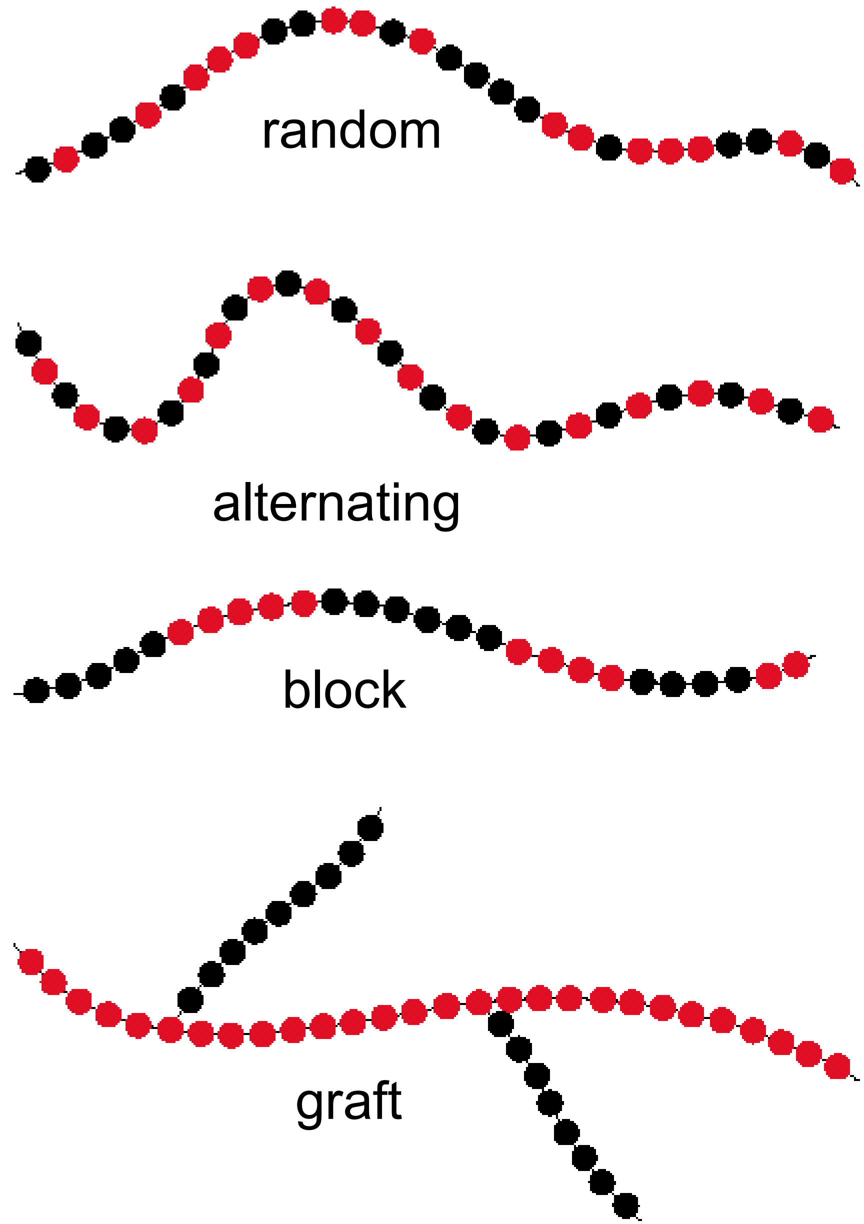
- Thermosets:
  --large cross linking
  (10 to 50% of mers)
  --hard and brittle
  --do NOT soften with heating
  --vulcanized rubber, epoxies,
  polyester resin, phenolic resin

# Copolymers

two or more monomers polymerized together

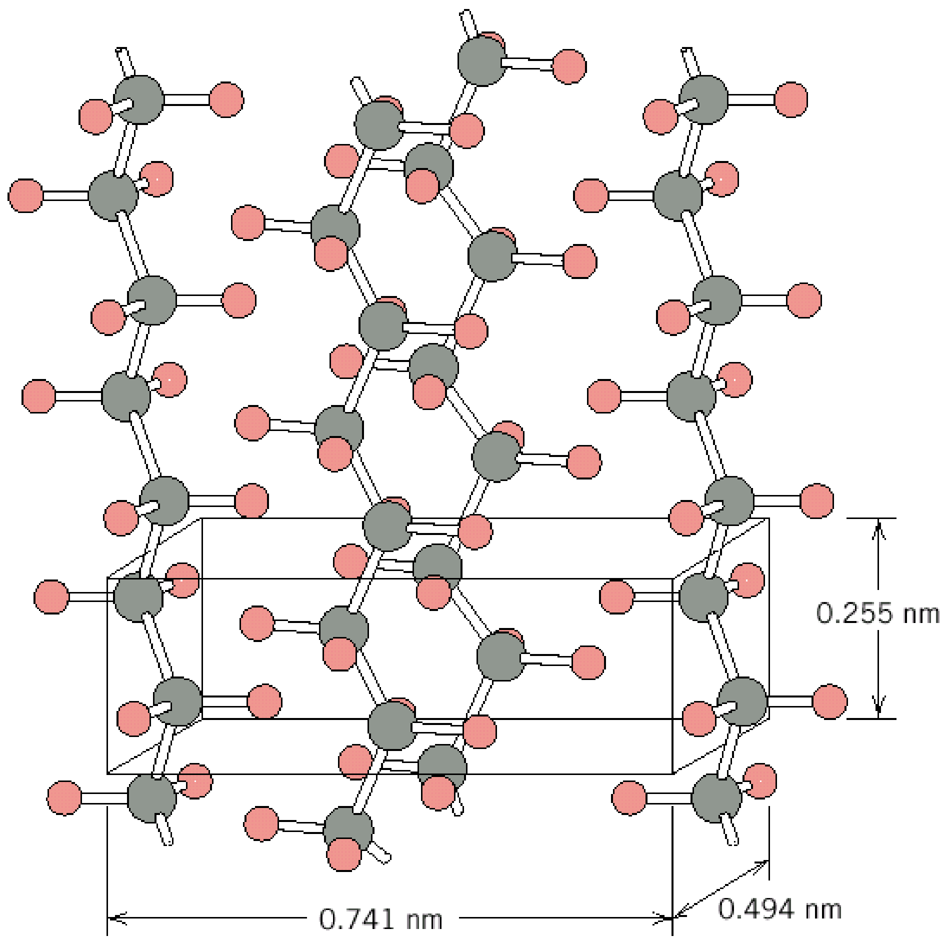
- random – A and B randomly positioned along chain
- alternating – A and B alternate in polymer chain
- block – large blocks of A units alternate with large blocks of B units
- graft – chains of B units grafted onto A backbone

A – ● B – ●



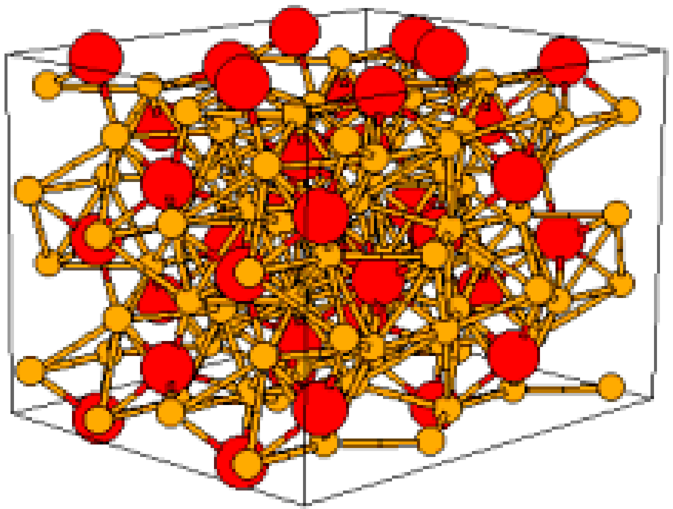
# Crystallinity in Polymers

- The crystalline state may exist in polymeric materials.
- However, since it involves molecules instead of just atoms or ions, as with metals or ceramics, the atomic arrangement will be more complex for polymers.
- There are ordered atomic arrangements involving molecular chains.
- Example shown is a polyethylene unit cell **(orthorhombic).**



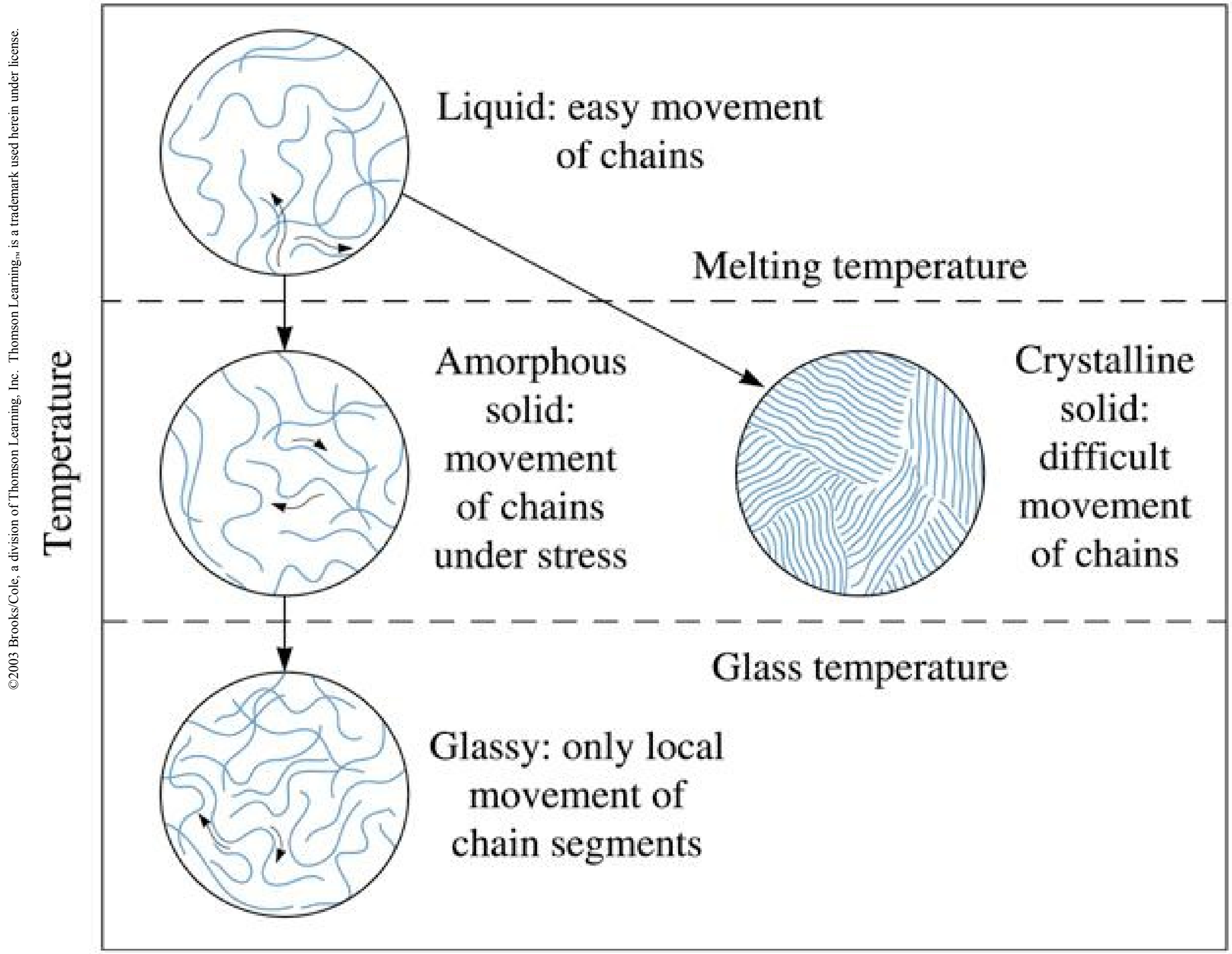
# Crystal Structures

| Polymer | Crystal Structure | Lattice Parameters (nm) |
|---|---|---|
| Polyethylene | Orthorhombic | $a_0 = 0.742$ $b_0 = 0.495$ $c_0 = 0.255$ |
| Polypropylene | Orthorhombic | $a_0 = 1.450$ $b_0 = 0.569$ $c_0 = 0.740$ |
| Polyvinyl chloride | Orthorhombic | $a_0 = 1.040$ $b_0 = 0.530$ $c_0 = 0.510$ |
| Polyisoprene (cis) | Orthorhombic | $a_0 = 1.246$ $b_0 = 0.886$ $c_0 = 0.810$ |



$Fe_3C$ – iron carbide – orthorhombic crystal structure

The effect of temperature on the structure and behavior of thermoplastics.

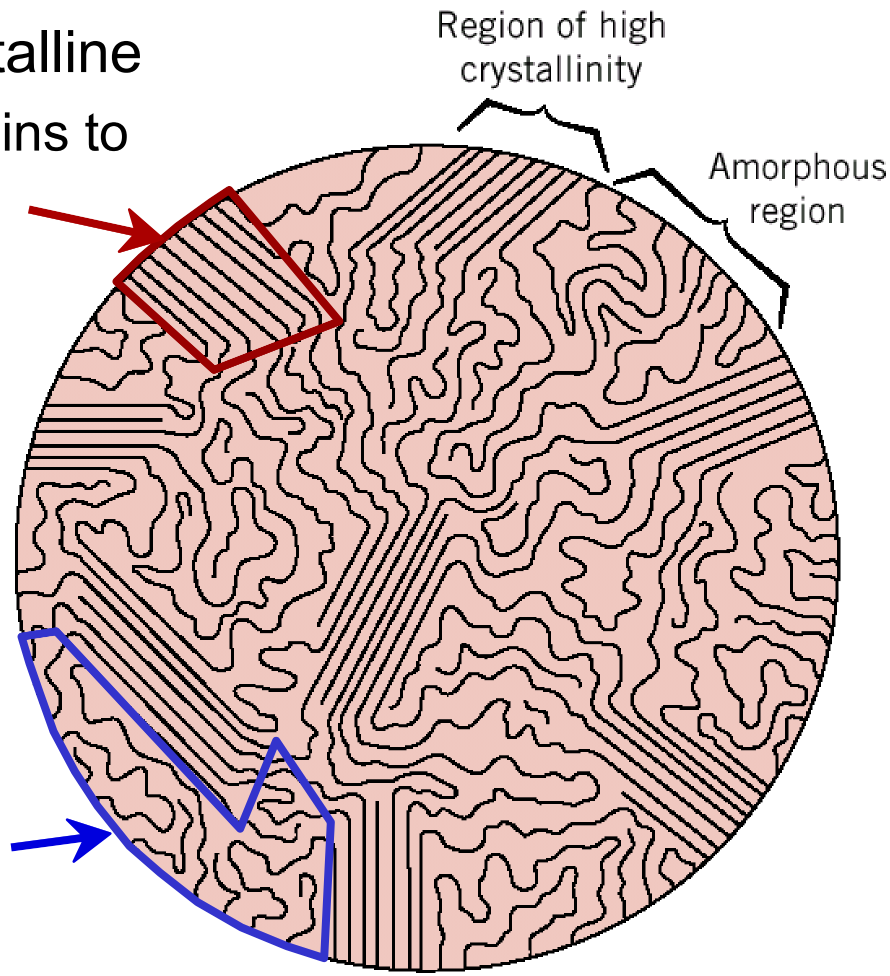


# Polymer Crystallinity

Polymers are rarely 100% crystalline

- Difficult for all regions of all chains to become aligned

- Degree of crystallinity expressed as % crystallinity.
  -- Some physical properties depend on % crystallinity.
  -- Heat treating causes crystalline regions to grow and % crystallinity to increase.



# Plastic Recycling Symbols

In 1988 the Society of the Plastics Industry developed a numeric code to provide a uniform convention for different types of plastic containers.

These numbers can be found on the underside of containers.

1. PET; PETE (polyethylene terephthalate): plastic water and soda bottles.
2. HDPE (high density polyethylene): laundry/dish detergent
3. V (Vinyl) or PVC: Pipes, shower curtains
4. LDPE (low density polyethylene): grocery bags, sandwich bags
5. PP (polypropylene): Tupperware®, syrup bottles, yogurt cups,
6. PS (polystyrene): Coffee cups, disposable cutlery
7. Miscellaneous: any combination of 1-6 plastics

1 PETE

2 HDPE

3 V

4 LDPE

5 PP

6 PS

7 OTHER

# Paper or Plastic?

- We live in a plastic society.
- Everything around us is plastic.
- Could you go for a day without plastic?
- Toothbrush, clothing, food containers, cooking spatulas, pans, bottled water, automobile parts, bicycle parts, eye glasses, iPod, calculator, mouse, computer parts, printer, stapler, head phones, TV, clock, flash memory housing, usb connector, keyboard, shoes, backpack parts, cell phone, credit cards..