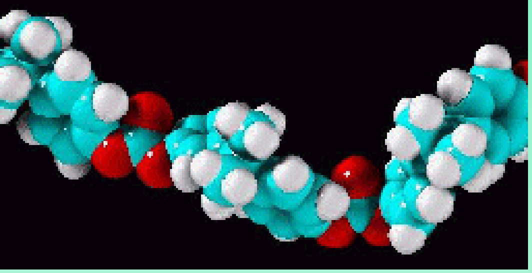
CHAPTERS 14/15:
POLYMER STRUCTURES, APPLICATIONS, & PROCESSING

ISSUES TO ADDRESS...

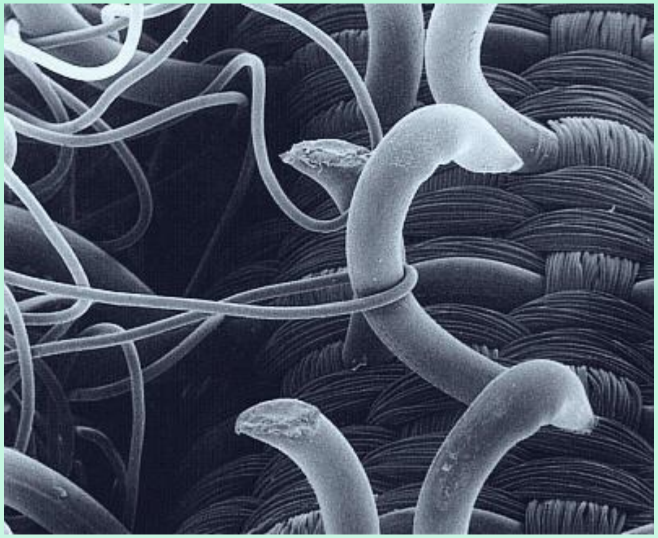
- What are the basic microstructural features?
- How do these features dictate room T tensile response?
- Hardening, anisotropy, and annealing in polymers.
- How does the mechanical response compare between ceramics and metals at elevated temperatures?



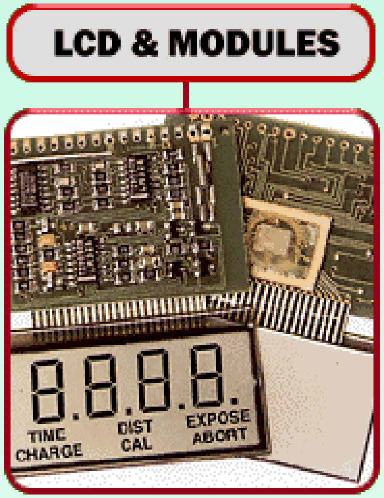
POLYMERS

Polymers are materials comprised of long molecular chains. Most polymers are carbon based and have relatively low melting points.

Typical plastic extrusion products.

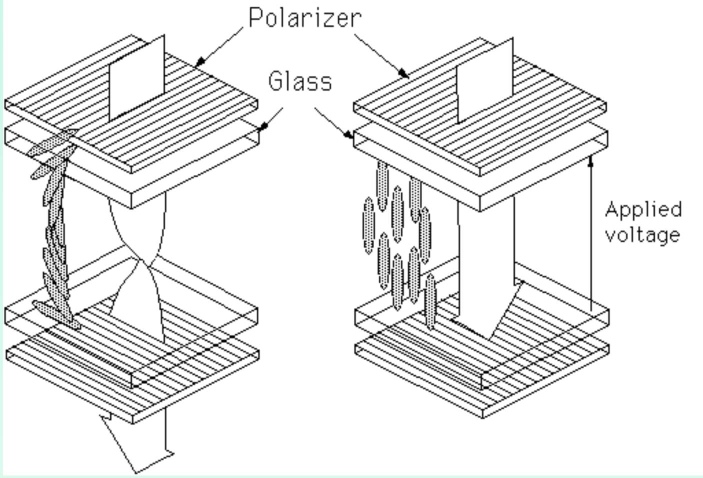


Synthetic fabrics are man-made copies of natural fabrics (Velcro).



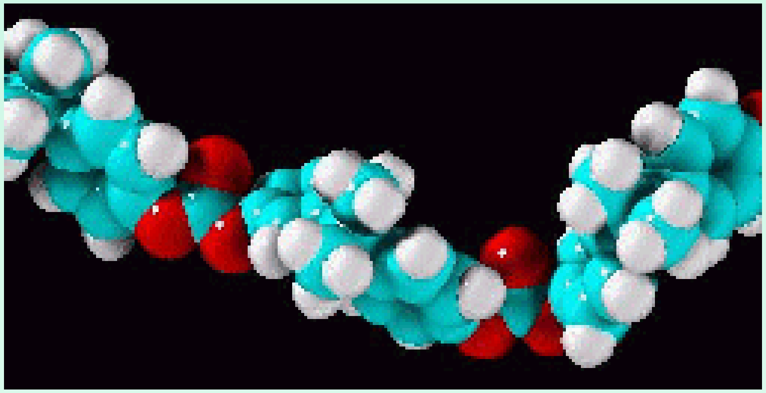
Liquid crystals are also polymers.

The principle of operation of a LCD



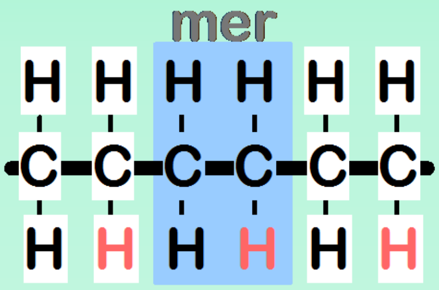
POLYMERS

- **A polymer** is a macromolecule (long molecules) built of small **covalently bonded** units called **monomers** ("mer" from the Greek word *meros* meaning part).
- These small units are repeated throughout the macromolecule chain.
- The macromolecules are bonded together by weak Van der Waals and hydrogen (secondary) bonds, or additional covalent cross-links.

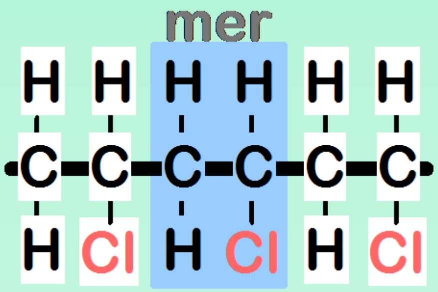


POLMER MICROSTRUCTURE

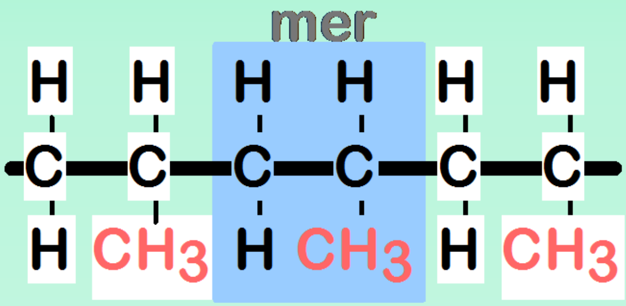
- Polymer = many mers



Polyethylene (PE)

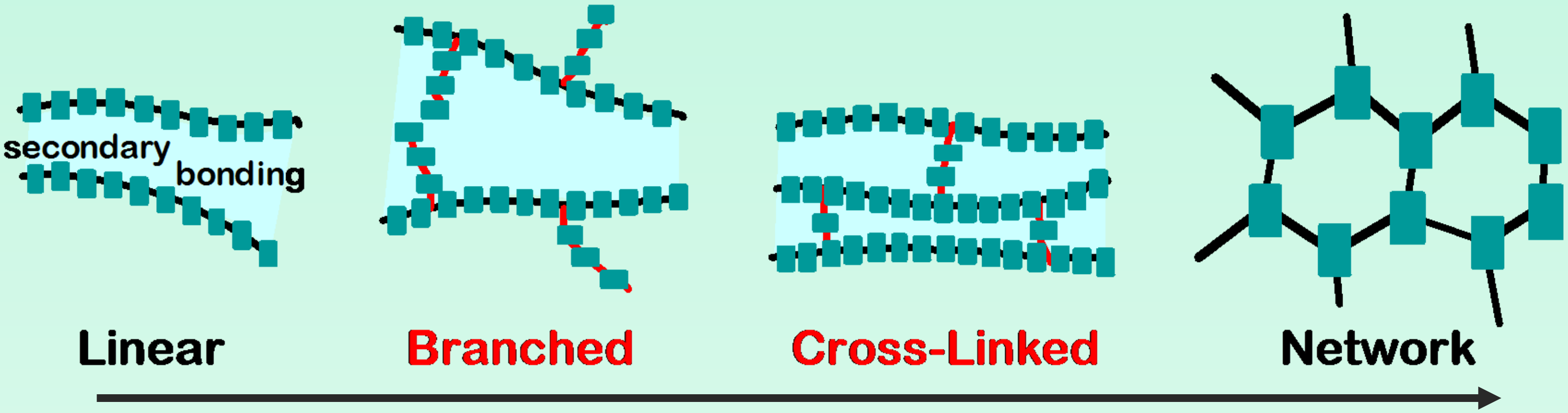


Polyvinyl chloride (PVC)



Polypropylene (PP)

- Covalent chain configurations and strength:



Direction of increasing strength

The Polymers: Classification

The ***main classes*** of polymers are:

- **Natural polymers**

  Example: *cellulose and protein*, which provide the mechanical basis for most plant and animal life

- **Thermoplastics**, which soften on heating

  Example: *polyethylene*

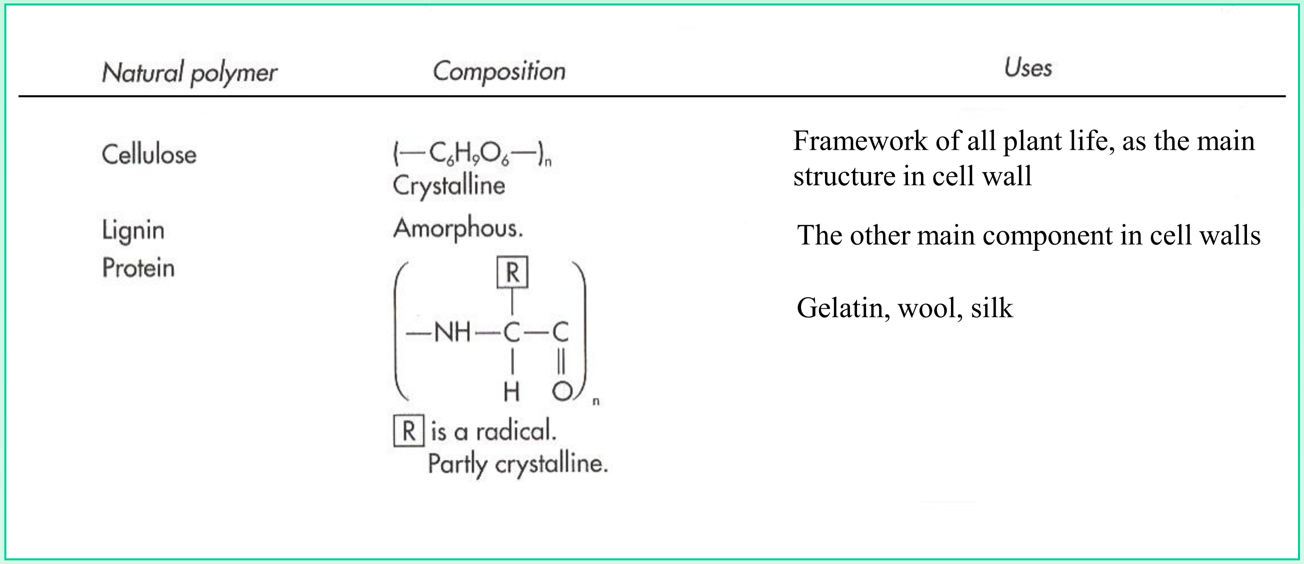
- **Thermosets** or **Resins**, which harden when two components are heated together

  Example: an *epoxy*

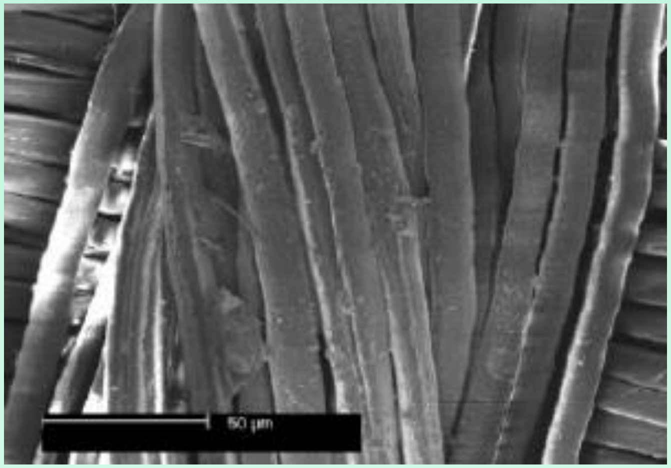
- **Elastomers or Rubbers**

Natural Polymers

- Polymers may be **natural**, such as *cellulose*, DNA, *caoutchouc* (India rubber).
- Living organisms are mainly composed of polymerized amino acids (proteins) nucleic acids (RNA and DNA), and other *biopolymers*.
- The most powerful computers -our brains - are mostly just a complex polymer material soaking in salty water!

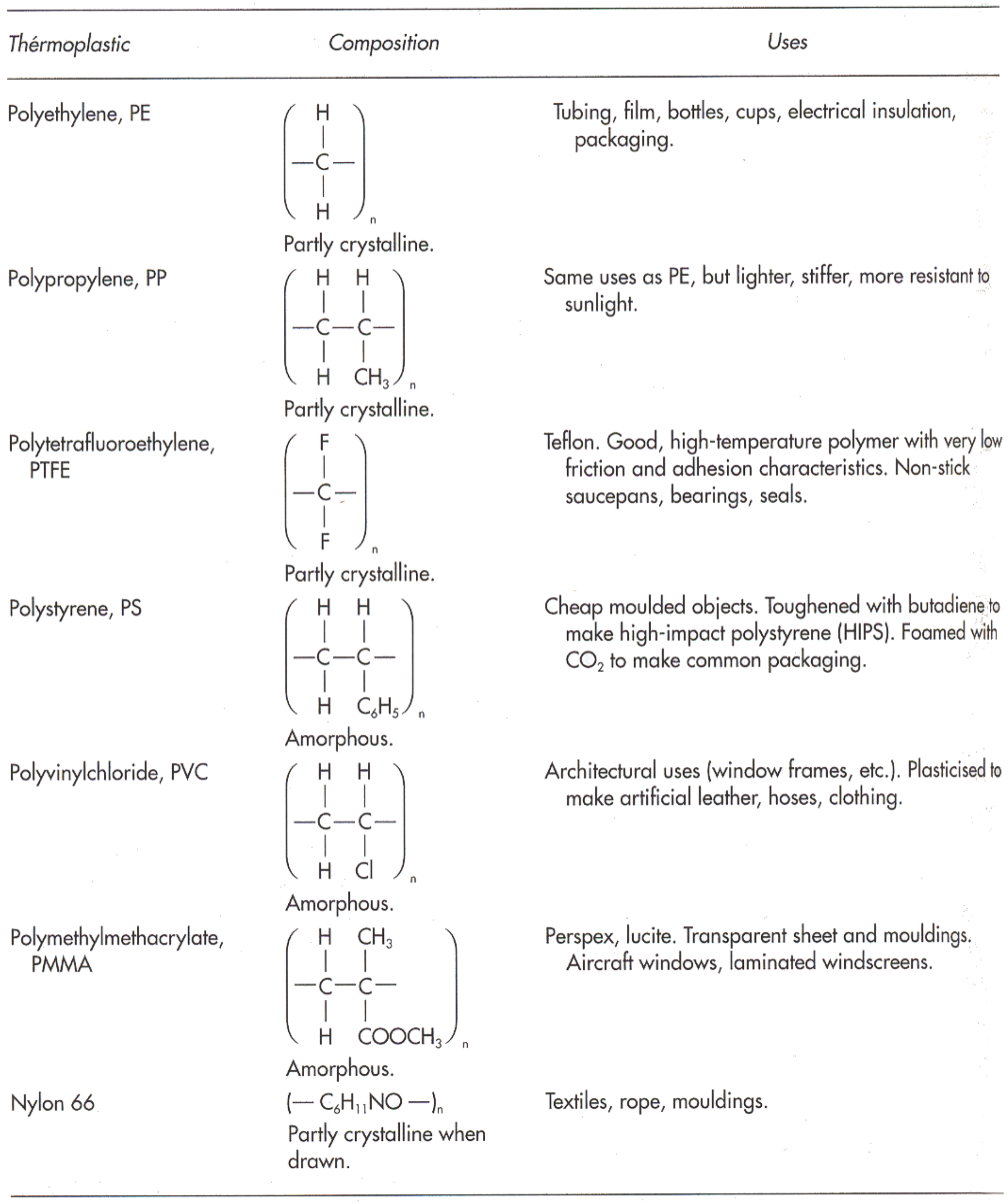


Natural polymer	*Composition*	*Uses*
Cellulose	$(-C_6H_9O_6-)_n$ Crystalline	Framework of all plant life, as the main structure in cell wall
Lignin	Amorphous.	The other main component in cell walls
Protein	$\left(-NH-\underset{H}{\overset{\boxed{R}}{C}}-\underset{O}{\overset{}{C}}\right)_n$ $\boxed{R}$ is a radical. Partly crystalline.	Gelatin, wool, silk



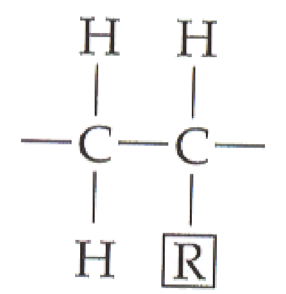
Silk fiber is produced by silk worms in a cocoon, to protect the silk-worm while it metamorphoses into a moth

Generic Thermoplastics



Thermoplastic	*Composition*	*Uses*
Polyethylene, PE	$\left(-\overset{H}{\underset{H}{\mathrm{C}}}- \right)_n$ Partly crystalline.	Tubing, film, bottles, cups, electrical insulation, packaging.
Polypropylene, PP	$\left(-\overset{H}{\underset{H}{\mathrm{C}}}-\overset{H}{\underset{CH_3}{\mathrm{C}}}- \right)_n$ Partly crystalline.	Same uses as PE, but lighter, stiffer, more resistant to sunlight.
Polytetrafluoroethylene, PTFE	$\left(-\overset{F}{\underset{F}{\mathrm{C}}}- \right)_n$ Partly crystalline.	Teflon. Good, high-temperature polymer with very low friction and adhesion characteristics. Non-stick saucepans, bearings, seals.
Polystyrene, PS	$\left(-\overset{H}{\underset{H}{\mathrm{C}}}-\overset{H}{\underset{C_6H_5}{\mathrm{C}}}- \right)_n$ Amorphous.	Cheap moulded objects. Toughened with butadiene to make high-impact polystyrene (HIPS). Foamed with CO_2 to make common packaging.
Polyvinylchloride, PVC	$\left(-\overset{H}{\underset{H}{\mathrm{C}}}-\overset{H}{\underset{Cl}{\mathrm{C}}}- \right)_n$ Amorphous.	Architectural uses (window frames, etc.). Plasticised to make artificial leather, hoses, clothing.
Polymethylmethacrylate, PMMA	$\left(-\overset{H}{\underset{H}{\mathrm{C}}}-\overset{CH_3}{\underset{COOCH_3}{\mathrm{C}}}- \right)_n$ Amorphous.	Perspex, lucite. Transparent sheet and mouldings. Aircraft windows, laminated windscreens.
Nylon 66	$(-C_6H_{11}NO-)_n$ Partly crystalline when drawn.	Textiles, rope, mouldings.

•**Thermoplastics** are made by adding together, i.e. "**polymerizing**", sub-units (monomers) to form long chain. Many of them are made of the unit:

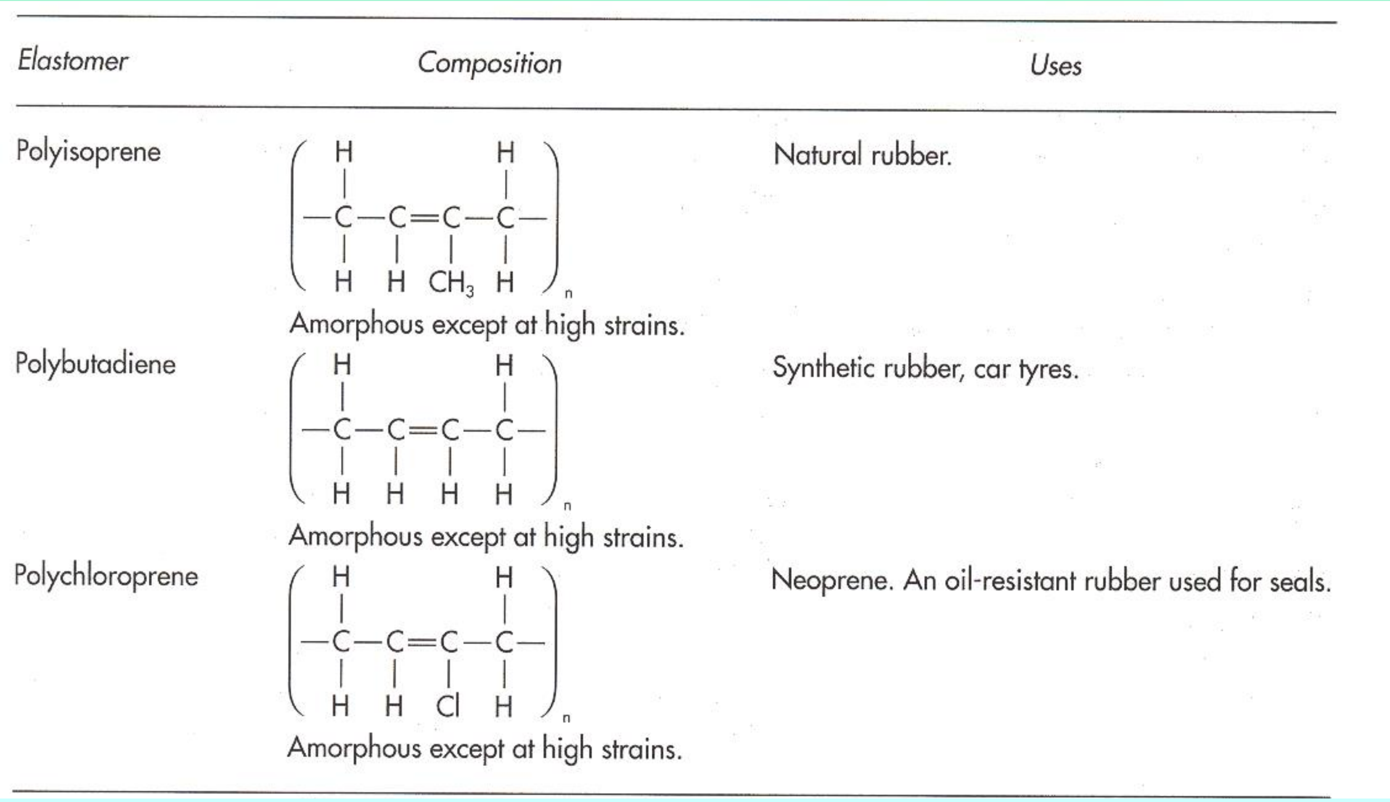


$$-\overset{H}{\underset{H}{\mathrm{C}}}-\overset{H}{\underset{\boxed{R}}{\mathrm{C}}}-$$

repeated many times.

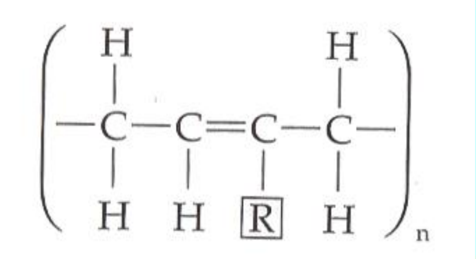
•The radical R may be hydrogen (PE) or $-CH_3$ (PP) or –Cl (PVC) or more complicated (as for nylon)

Generic Elastomers (Rubbers)



Elastomer	*Composition*	*Uses*
Polyisoprene	$\left(-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\mathrm{C}}=\underset{\mathrm{CH_3}}{\mathrm{C}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}- \right)_n$ Amorphous except at high strains.	Natural rubber.
Polybutadiene	$\left(-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\mathrm{C}}=\underset{\mathrm{H}}{\mathrm{C}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}- \right)_n$ Amorphous except at high strains.	Synthetic rubber, car tyres.
Polychloroprene	$\left(-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\mathrm{C}}=\underset{\mathrm{Cl}}{\mathrm{C}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}- \right)_n$ Amorphous except at high strains.	Neoprene. An oil-resistant rubber used for seals.

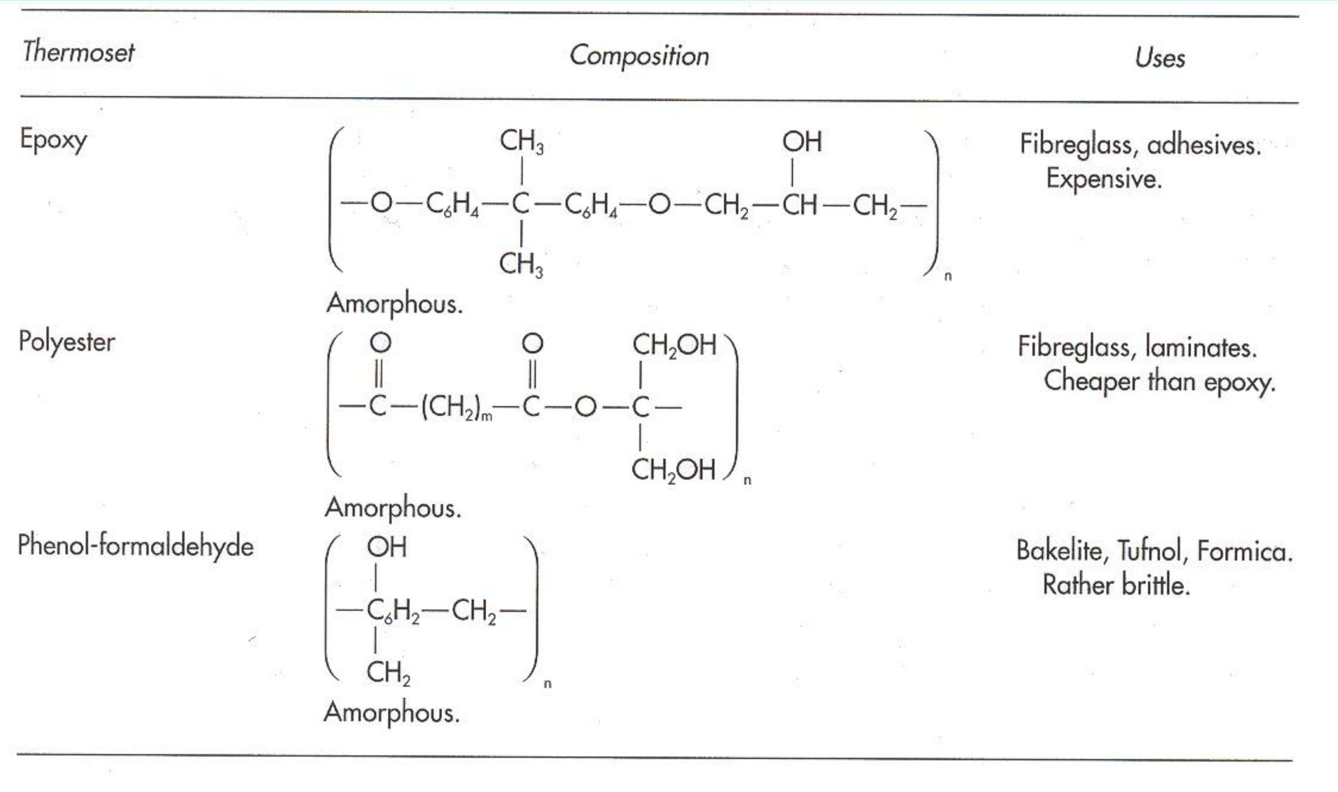
- Rubbers are almost-**linear polymers** with occasional cross-linked in which at room temperature the secondary bonds have already melted.
- However the cross-linked provide “memory” of the material so that it returns to its original shape on unloading.
- The common rubbers are all based on a **single structure**:



$$\left(-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\mathrm{C}}=\underset{\boxed{\mathrm{R}}}{\mathrm{C}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}- \right)_n$$

with the position **R** occupied by H, CH_3 or Cl.

Generic Resins



Thermoset	*Composition*	*Uses*
Epoxy	$\left(-O-C_6H_4-\overset{CH_3}{\underset{CH_3}{C}}-C_6H_4-O-CH_2-\overset{OH}{CH}-CH_2- \right)_n$ Amorphous.	Fibreglass, adhesives. Expensive.
Polyester	$\left(-\overset{O}{\overset{\|}{C}}-(CH_2)_m-\overset{O}{\overset{\|}{C}}-O-\overset{CH_2OH}{\underset{CH_2OH}{C}}- \right)_n$ Amorphous.	Fibreglass, laminates. Cheaper than epoxy.
Phenol-formaldehyde	$\left(-\overset{OH}{\underset{CH_2}{C_6H_2}}-CH_2- \right)_n$ Amorphous.	Bakelite, Tufnol, Formica. Rather brittle.

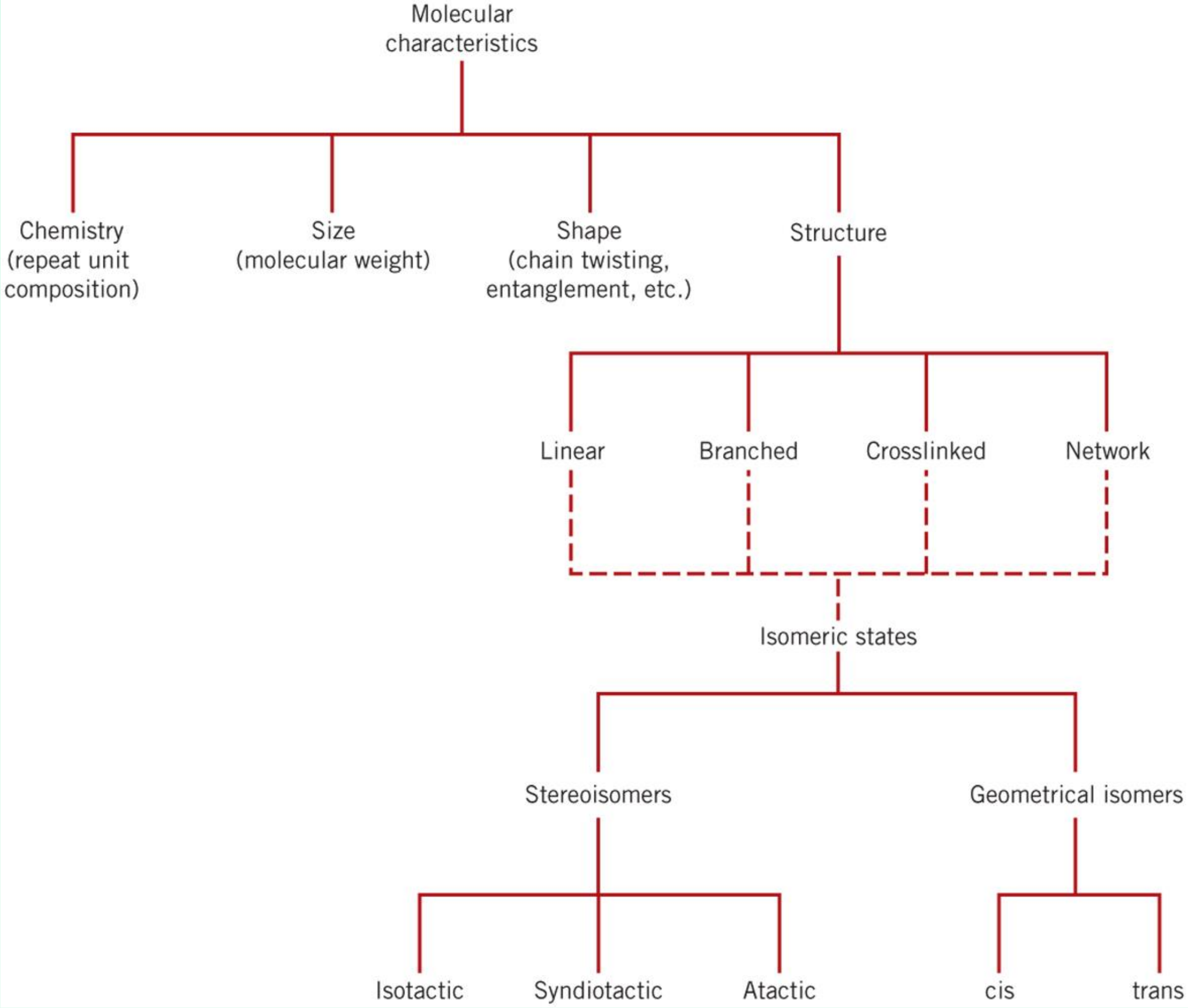
- Epoxy: an adhesive and a matrix for different composites is a thermoset.

- Thermosets are made by mixing of two components (a resin and a harder) which react and harden, either at room temperature or on heating

- The resulting polymers is usually heavily cross-linked: **network polymer**!!

- The cross-links form during the polymerization of the liquid resin and hardener so the structure is almost **amorphous.**

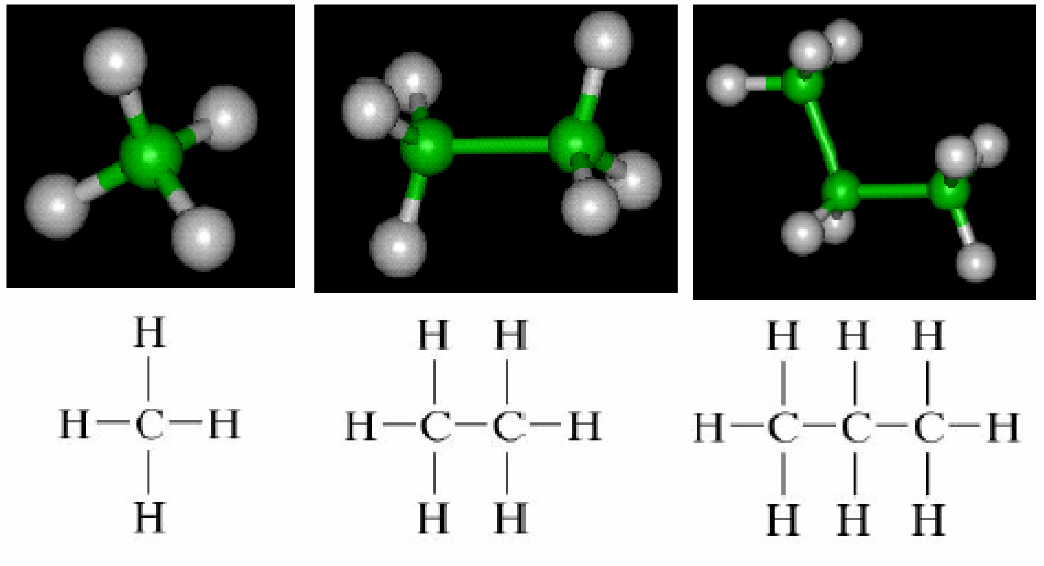
Polymer Characteristics



THE STRUCTURE of POLYMERS:

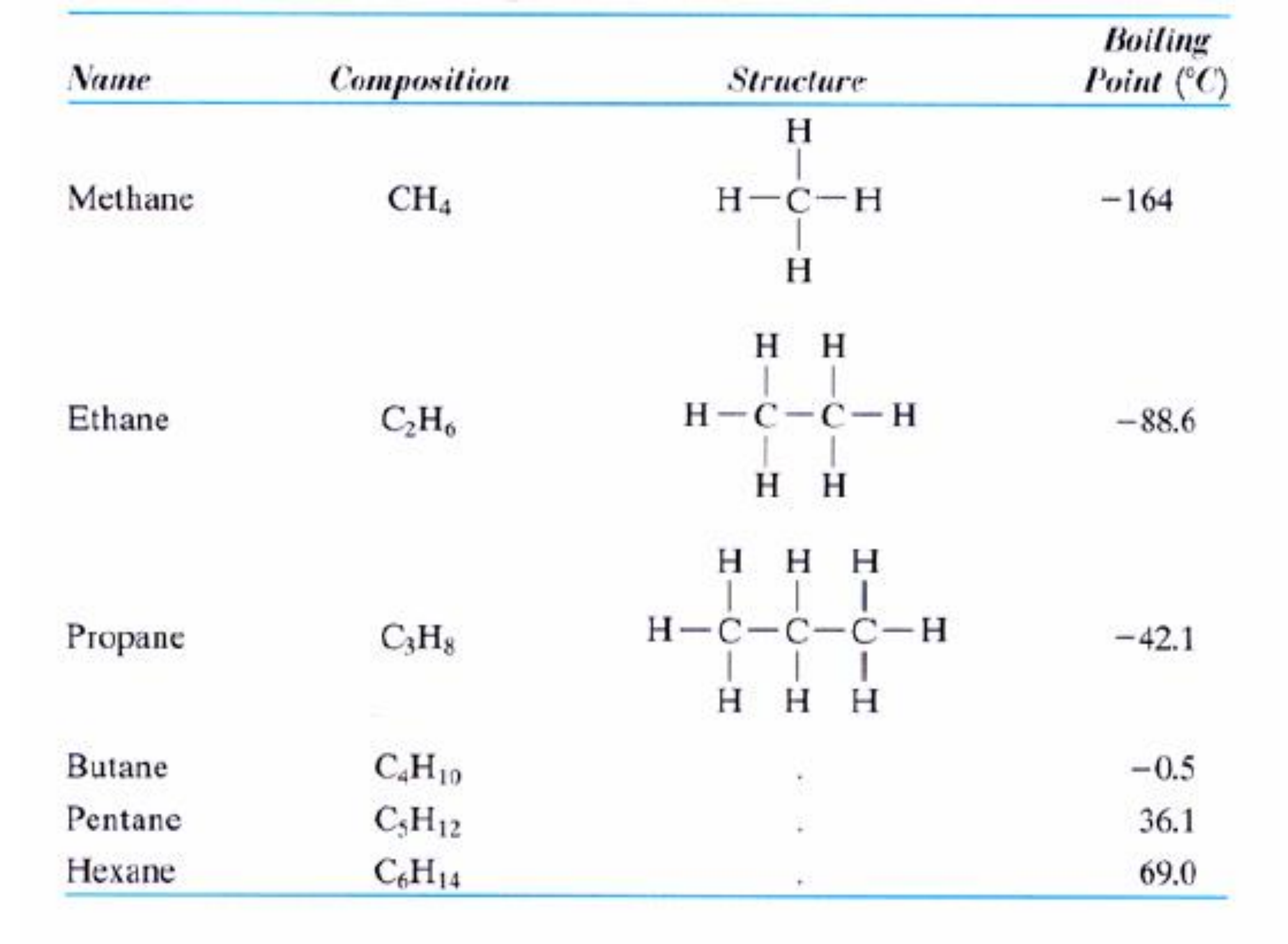
Hydrocarbon Molecules

- 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-
- Attachment of different organic groups to the hydrocarbon backbone offers wide variety of possible polymers
- Examples of **saturated** (all bonds are single ones) hydrocarbon molecules (of type C_nH_{2n+2})



Methane, CH_4 Ethane, C_2H_6 Propane, C_3H_8

Compositions and Molecular Structures for some C_nH_{2n+2} Compounds

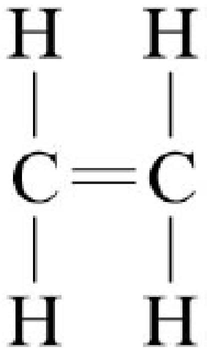


Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4	$H-\overset{H}{\underset{H}{C}}-H$	−164
Ethane	C_2H_6	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	−88.6
Propane	C_3H_8	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	−42.1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

Boiling Points rise

Unsaturated Bonds

Double and triple bonds can exist between C atoms (sharing of two or three electron pairs). These bonds are called **unsaturated bonds.** Unsaturated molecules are more reactive



$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

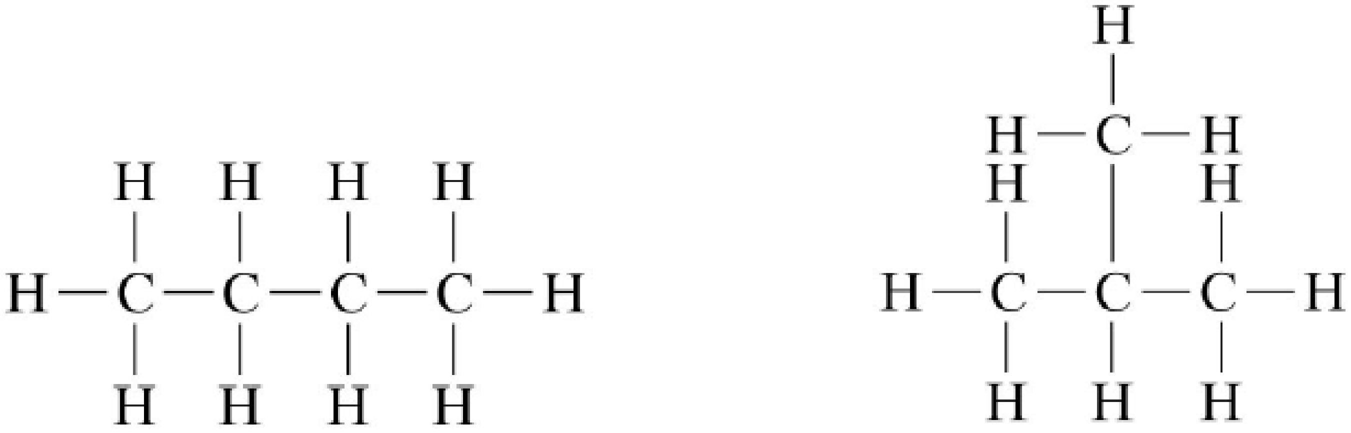
Ethylene, C_2H_4

$$H-C\equiv C-H$$

Acetylene, C_2H_2

ISOMERS

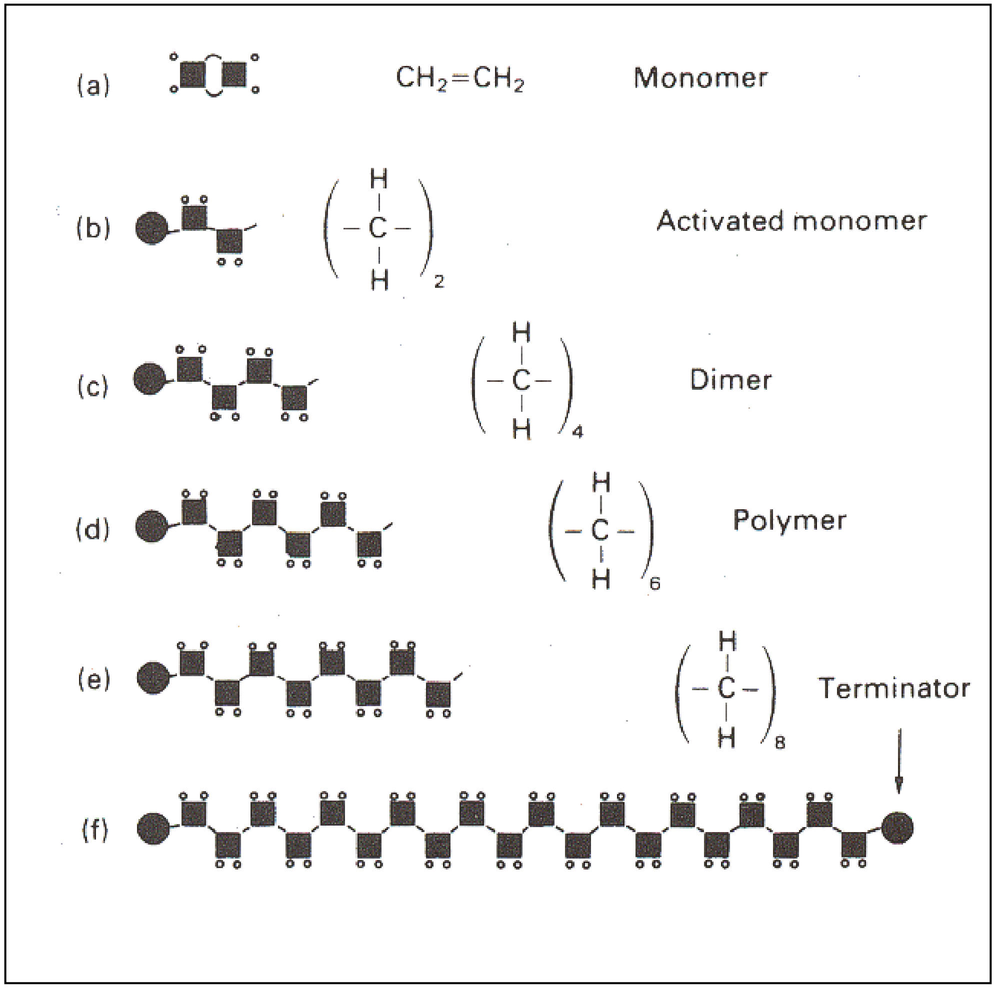
Isomers are molecules that contain the same atoms but in a different arrangement. An example is butane and **isobutane**:



Butane → C_4H_{10} ← Isobutane

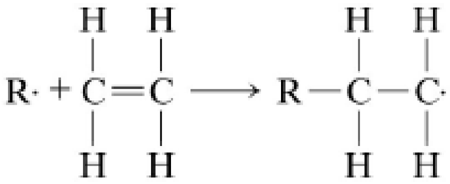
The Polymers Chemistry: Ethylene →Polyethylene

- **Polymerization**: the reaction of the monomers to form the polymer macromolecule



(a) The initial monomer (R);

(b) Under certain conditions (T, P) in the presence of *catalyst* the double bonds break:



$$R\cdot + \underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}} \longrightarrow R-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\cdot$$

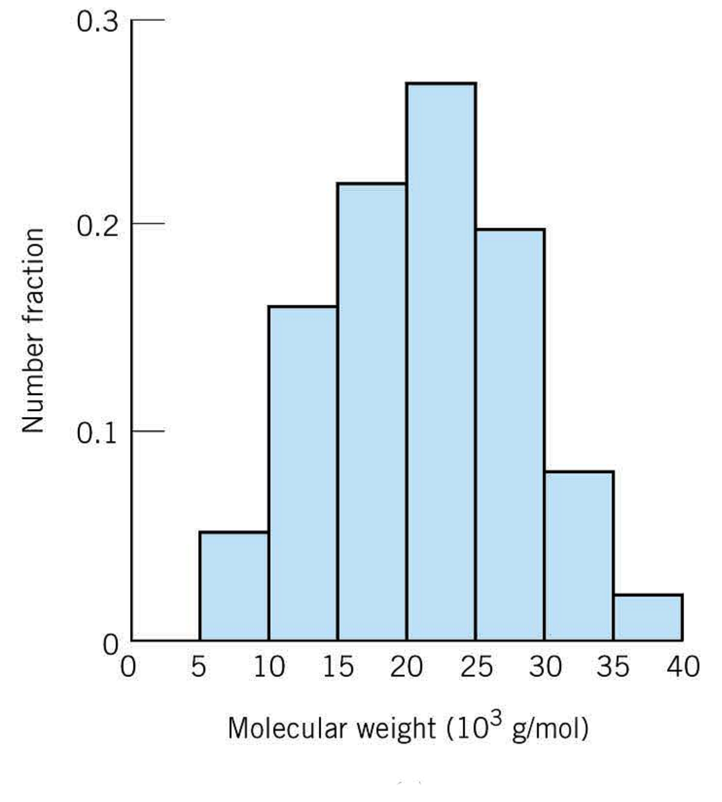
forming a highly reactive radical with an unpaired electron, ready for the linking (polymerization)

(d-f) the ethylene polymer (polyethylene) chain is limited by the addition of *terminators* (e.g. –OH group).

Molecular Weight (1)

To create a solid with useful mechanical properties the chain must be long !!

One may describe chain length in terms of polymer **average molecular weight,** which can be defined in several ways:



(1) A **number-average molecular weight** M_n : divide chains into series of size ranges and then determine the number fraction x_i of each size range

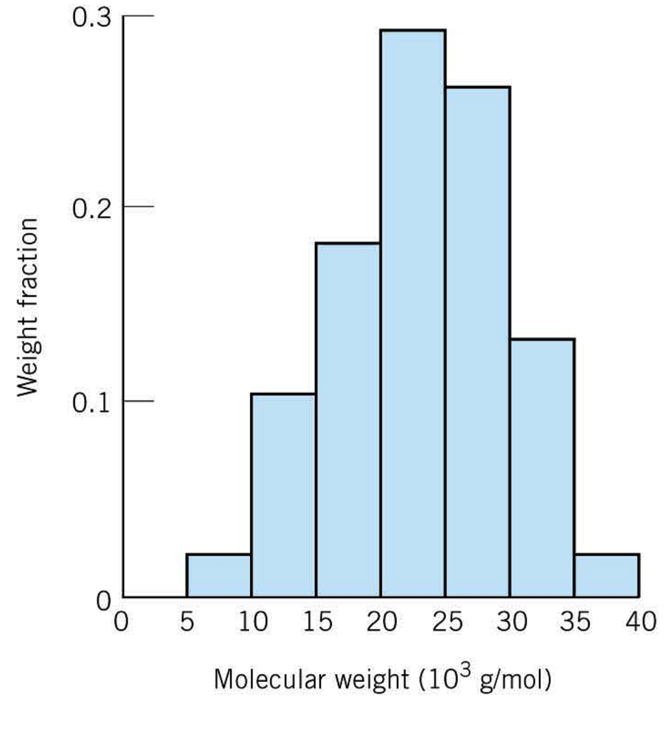
$$\overline{M_n} = \sum x_i M_i$$

where M_i represents the mean molecular weight of the size range i, and x_i is the fraction of total number of chains within the corresponding size range

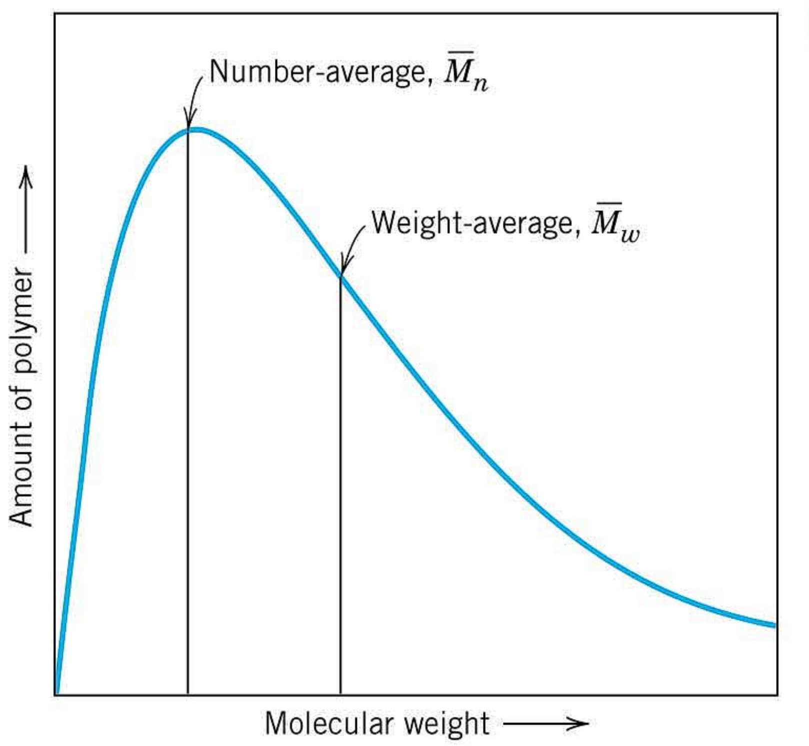
Molecular Weight (2)

(2) A **weight average molecular** weight M_w is based on the weight fraction w_i within the size ranges:

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



Typical distribution of molecular weight



Molecular Weight Calculation

Example: average mass of a class

Student	Weight
	mass (lb)
1	104
2	116
3	140
4	143
5	180
6	182
7	191
8	220
9	225
10	380

What is the average weight of the students in this class:

a) Based on the number fraction of students in each mass range?

b) Based on the weight fraction of students in each mass range?

Molecular Weight Calculation (cont.)

Solution: The first step is to sort the students into weight ranges. Using 40 lb ranges gives the following table:

weight range mass (lb)	number of students N_i	mean weight W_i mass (lb)
81-120	2	110
121-160	2	142
161-200	3	184
201-240	2	223
241-280	0	-
281-320	0	-
321-360	0	-
361-400	1	380

total number → SN_i

10

SN_iW_i ← total weight

1881

Calculate the number and weight fraction of students in each weight range as follows:

$$x_i = \frac{N_i}{\sum N_i} \qquad w_i = \frac{N_i W_i}{\sum N_i W_i}$$

For example: for the 81-120 lb range

$$X_{81-120} = \frac{2}{10} = 0.2$$

$$w_{81-120} = \frac{2 \text{ x } 110}{1881} = 0.117$$

Molecular Weight Calculation (cont.)

weight range mass (lb)	mean weight W_i mass (lb)	number fraction x_i	weight fraction w_i
81-120	110	0.2	0.117
121-160	142	0.2	0.150
161-200	184	0.3	0.294
201-240	223	0.2	0.237
241-280	-	0	0.000
281-320	-	0	0.000
321-360	-	0	0.000
361-400	380	0.1	0.202

$$\boxed{\overline{M}_n = \sum x_i M_i} = (0.2 \text{ x } 110 + 0.2 \text{ x } 142 + 0.3 \text{ x } 184 + 0.2 \text{ x } 223 + 0.1 \text{ x } 380) = \boxed{188 \text{ lb}}$$

$$\boxed{\overline{M}_w = \sum w_i M_i} = (0.117 \text{ x } 110 + 0.150 \text{ x } 142 + 0.294 \text{ x } 184$$

$$+ 0.237 \text{ x } 223 + 0.202 \text{ x } 380) = \boxed{218 \text{ lb}}$$

$$\overline{M}_w = \sum w_i M_i = 218 \text{ lb}$$

Degree of Polymerization (1)

The chain length in a polymer can also be described in terms of a **degree polymerization n**, which represents an average number of “mer” units in a chain

Again two approaches are possible:

Number average n_n:

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

where $\overline{m}$ is a mer molecular weight

Weight-average n_w:

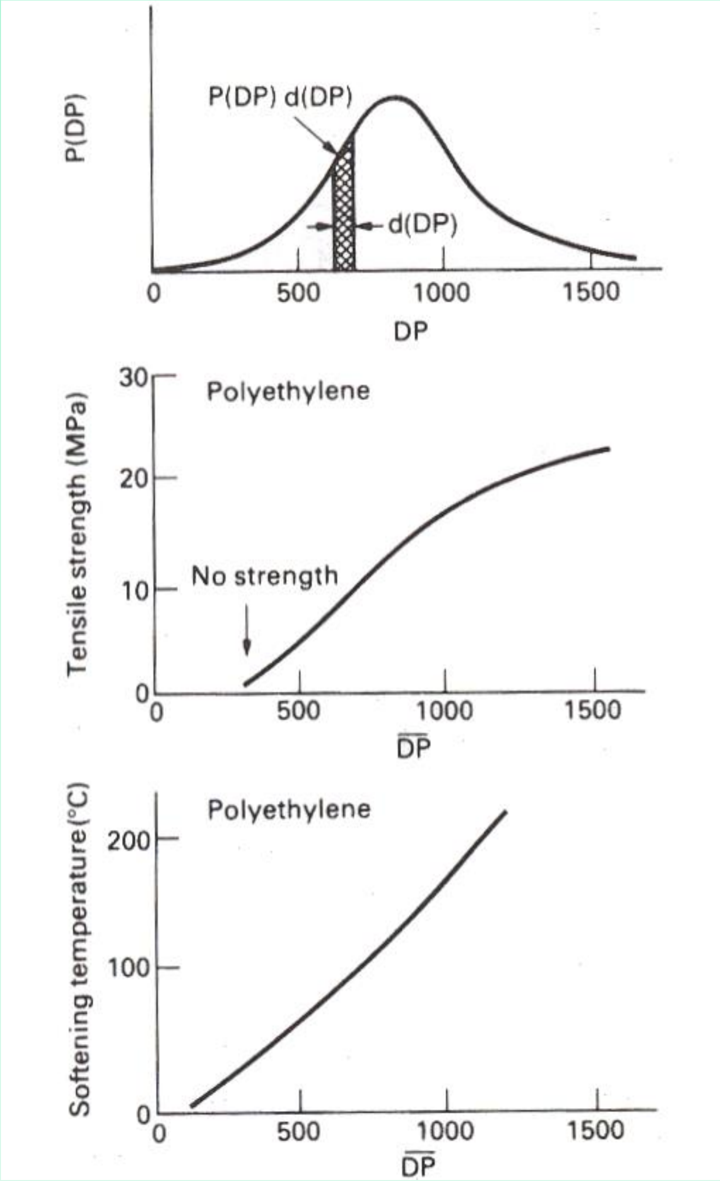
$$n_w = \frac{\overline{M}_w}{\overline{m}}$$

if the polymer is built up of different mer units (*copolymer*) $\overline{m}$ is determined from :

$$\overline{m} = \sum f_i m_i$$

where f_j and m_j are the chain fraction and molecular weight for mer j.

Degree of Polymerization (2)



Average $\overline{\mathbf{DP}}$ is simply:

$$\overline{DP} = \int_0^\infty DP \cdot P(DP)d(DP)$$

where P(DP)d(DP) is the fraction of molecules with DP values between DP and DP+d(DP).
And the molecular weight, M, is just

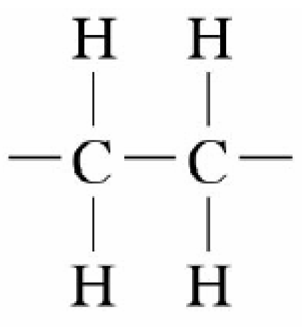
M=m·DP

where **m** is the molecular weight of monomer

Polymer properties depend on average DP.
<u>Example:</u> higher DP higher **tensile strength** and **melting point**!!
<u>Question</u>: how one can control DP ?!

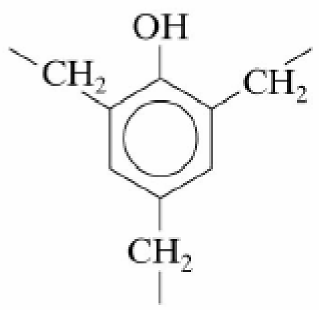
MOLECULAR ARCHITECTURE

- A molecule with <u>one</u> active bond can act as chain *terminator* **but** cannot form a link in a chain
  <u>Example</u>: -OH
- Monomers which form *linear chain* have <u>two active</u> bonds they are **bifunctional**. <u>Example:</u> thermoplastics have linear not cross-linked molecules (polyethylene)
- Monomers with <u>three or more</u> active sites (**polyfunctional**) form *network*.
  <u>Example:</u> thermosetting polymers



$$-\begin{array}{c}H\\|\\C\\|\\H\end{array}-\begin{array}{c}H\\|\\C\\|\\H\end{array}-$$

Ethylene



Phenol-formaldehyde

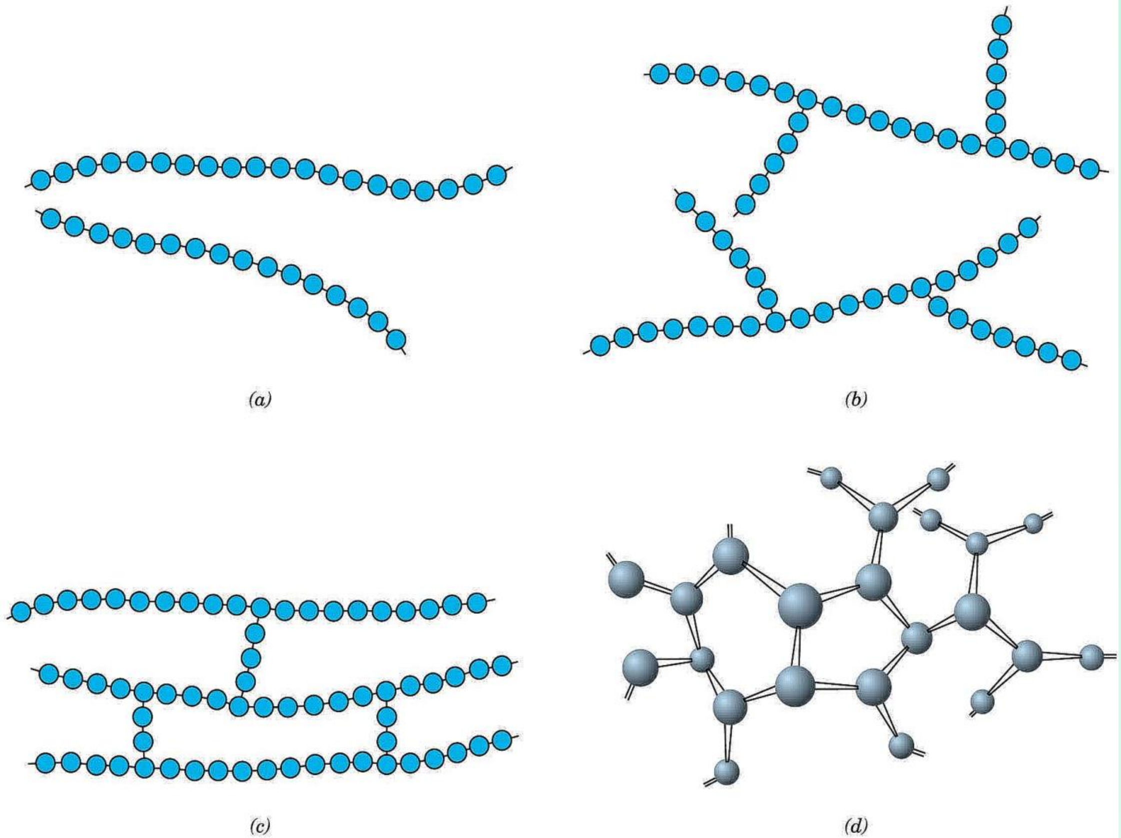
Molecular Structure

(a) **Linear Polymer**: end-to-end joining of mers, single, long flexible chains, van-der-Waals and hydrogen bonds hold chains together (polyethylene etc.)

(b) **Branched Polymer**: side branch chains connected to main chain, reduced chain packing capability and therefore density

(c) **Cross-Linked Polymers**: adjacent chains joined by side chains; synthesis at elevated temperatures promotes cross-linking; non-carbon atoms might be involved in cross-linking bond (e.g. sulfur in vulcanization, rubber)

(b) **Network-Polymers**: highly cross-linked, tri-functional mers can provide three dimensional cross-linking (epoxy resins, phenyl-formaldehyde)

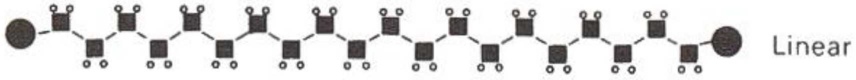


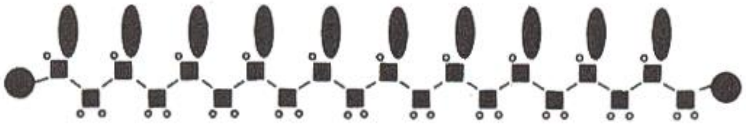
Stereoisomerism: thermoplastics

- Polyethylene is the simplest linear chain.

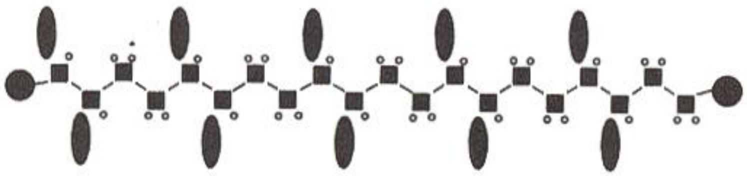
By replacing one H atom with a **side-group** or radical **R**→ a vinyl group of polymers
Example: R=Cl (Polyvinyl chloride) or R=CH_3 (polypropylene)

R gives asymmetry to the repeating units that causes more than one way in which they can be linked to **form** a chain – ***stereoisomerism.*** Transformation from one in to the other isomer is not possible by bond rotation.

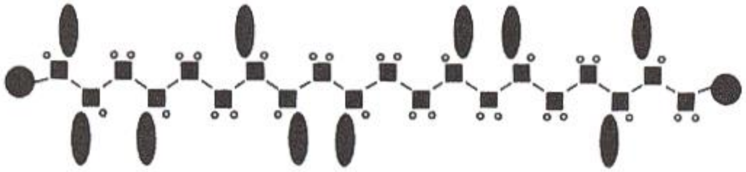




isotactic configuration: all R-groups are situated on the same side of the chain



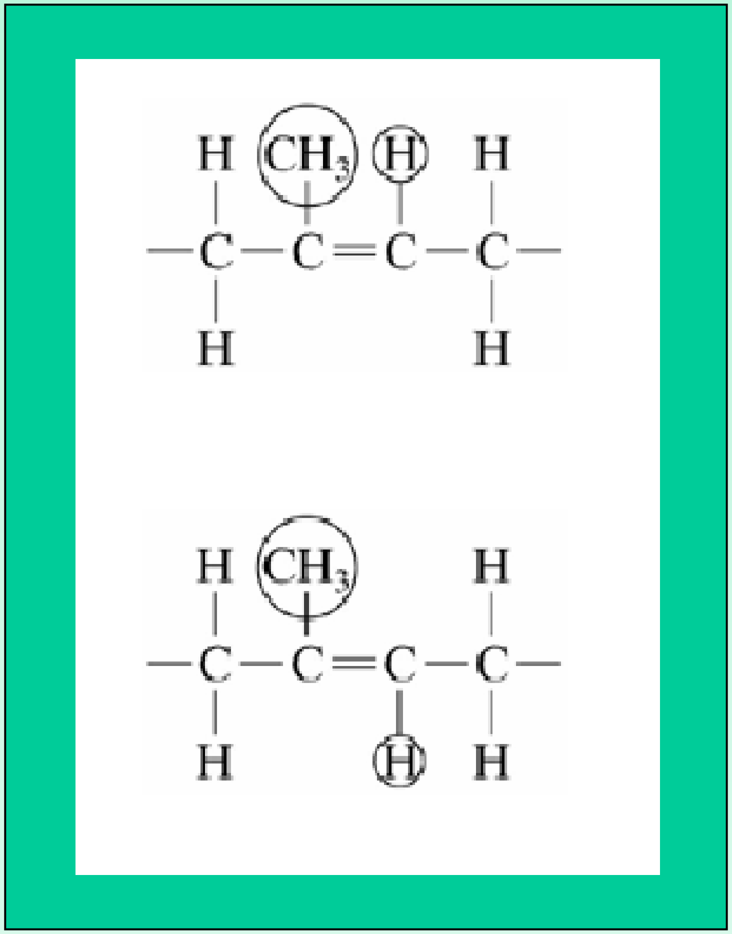
syndiotactic configuration: R-groups are situated on alternate sides of the chain



atactic configuration: R-groups are arranged in a random position

Geometrical Isomers: rubbers

- Consider a carbon-carbon double bond in rubbers, which cannot rotate freely without breaking a covalent bond, the R group or side-atom can be positioned on the same side (cis) or on opposite sides (trans).

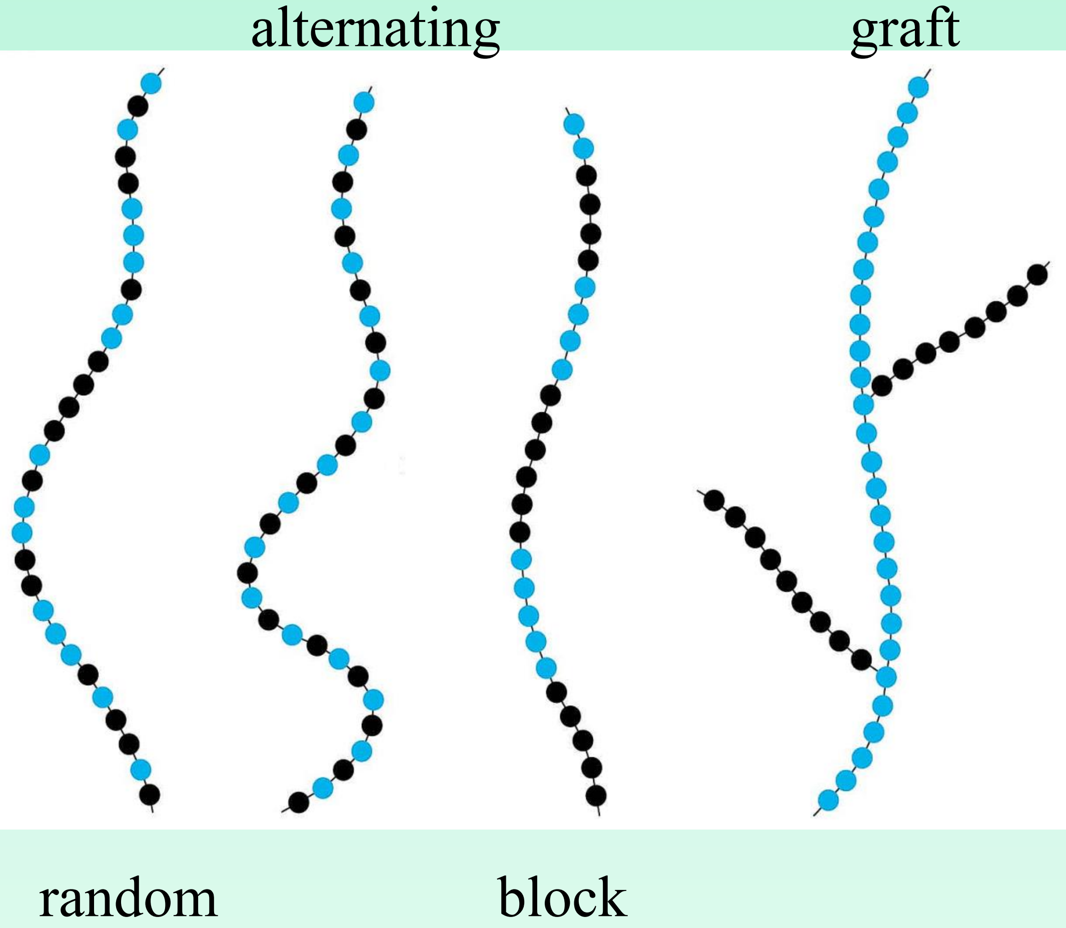


cis-polyisoprene (natural rubber) H and CH_3 group on the same side, the other bonds are along the chain

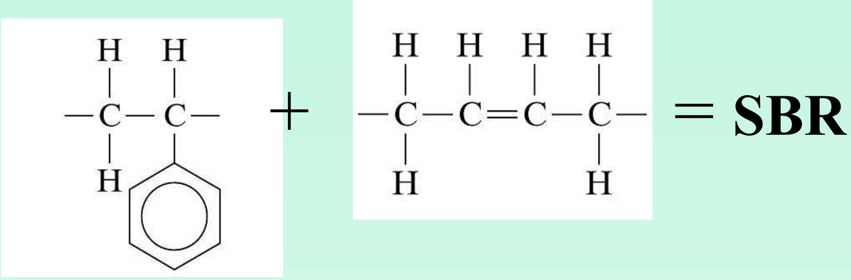
trans-polyisoprene properties differ markedly from natural rubber (“gutta percha”)

Copolymers

Copolymers consist of two or more ***different mer units***. An idea is similar to this for composites: obtain new polymer properties by combination!! Depending on the polymerization process and relative fraction of mer types different arrangements are possible.



Example: Styrene-butadiene rubber is a common synthetic copolymer For automobile tires

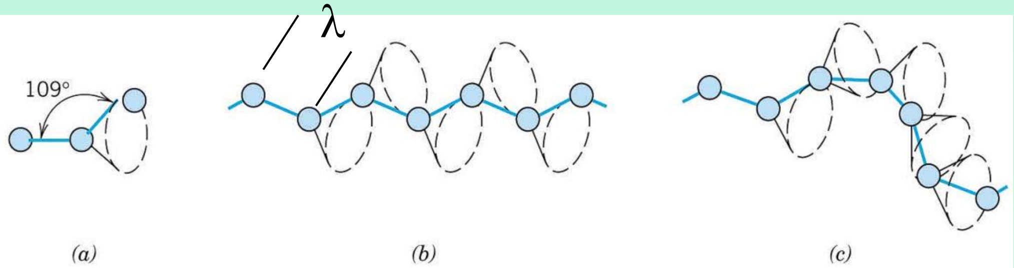


Styrene

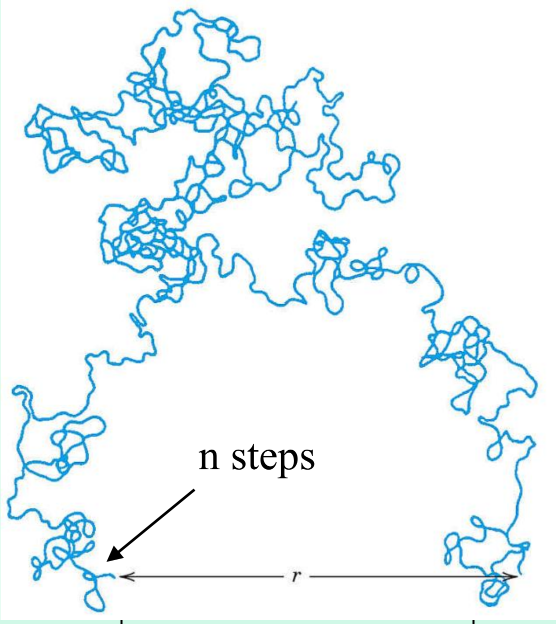
Butadiene

Molecular Shape

The *rotational degree of freedom* in the bonds of the polymer chain backbone allows a wide range of molecular shapes for the chain. One example in nature is the folding of proteins which influences the functionality of the whole structure.



Schematic representations of how polymer chain shape is influenced by the positioning of backbone carbon atoms (colored circles). For (*a*), the rightmost atom may lie anywhere on the dashed circle and still subtend a 109° angle with the bond between the other two atoms. Straight and twisted chain segments are generated when the backbone atoms are situated as in (*b*) and (*c*), respectively.



$$r = (\lambda)^{1/2} n$$

Because chain-links bend in a random way the average distance, r, between start and end of the chain calculated in the same way as the distance a drunk staggers from the pub (a “random walk”)

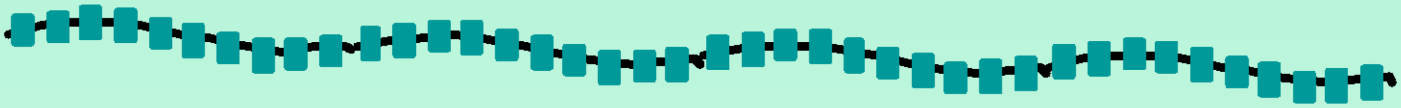
Polymer Crystallinity

Packing of the molecular chains
so as to produce an ordered atomic array

MOLECULAR WEIGHT & CRYSTALLINITY

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

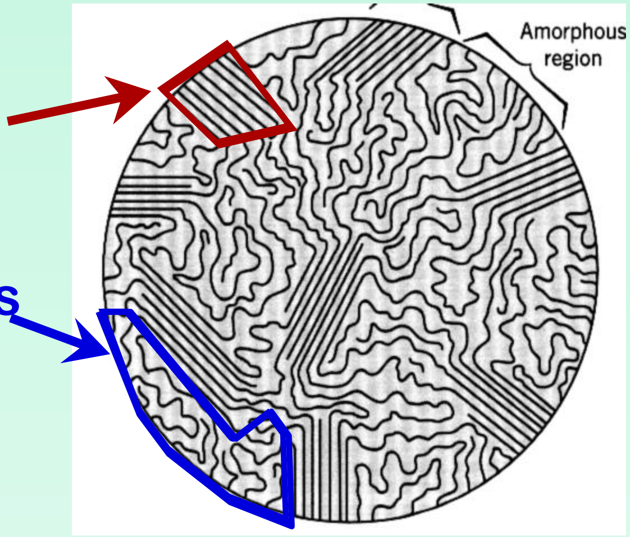
smaller M_w



larger M_w

- Tensile strength (TS):
  --often increases with M_w.
  --Why? Longer chains are entangled (anchored) better.

- **% Crystallinity**: % of material that is crystalline.
  --TS and E often increase
  with % crystallinity.
  --Annealing causes
  crystalline regions
  to grow. % crystallinity
  increases.



crystalline
region

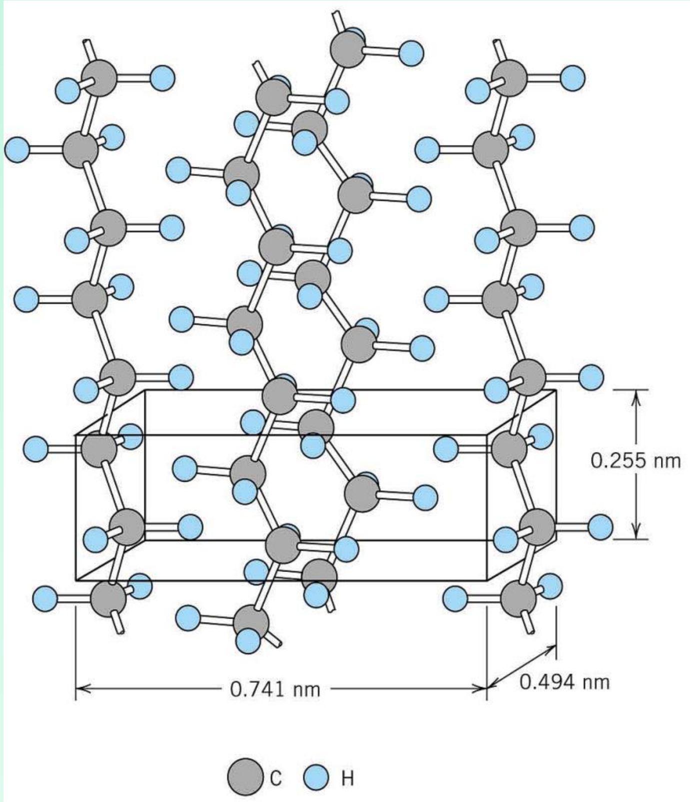
amorphous
region

POLYMER CRYSTALLINITY (1)

Reminder:

- *Crystalline structure:* arrangement of unit cells in a well-defined spatially-ordered manner, which is characterized by translational symmetry
- *Amorphous structures:* random arrangement of units

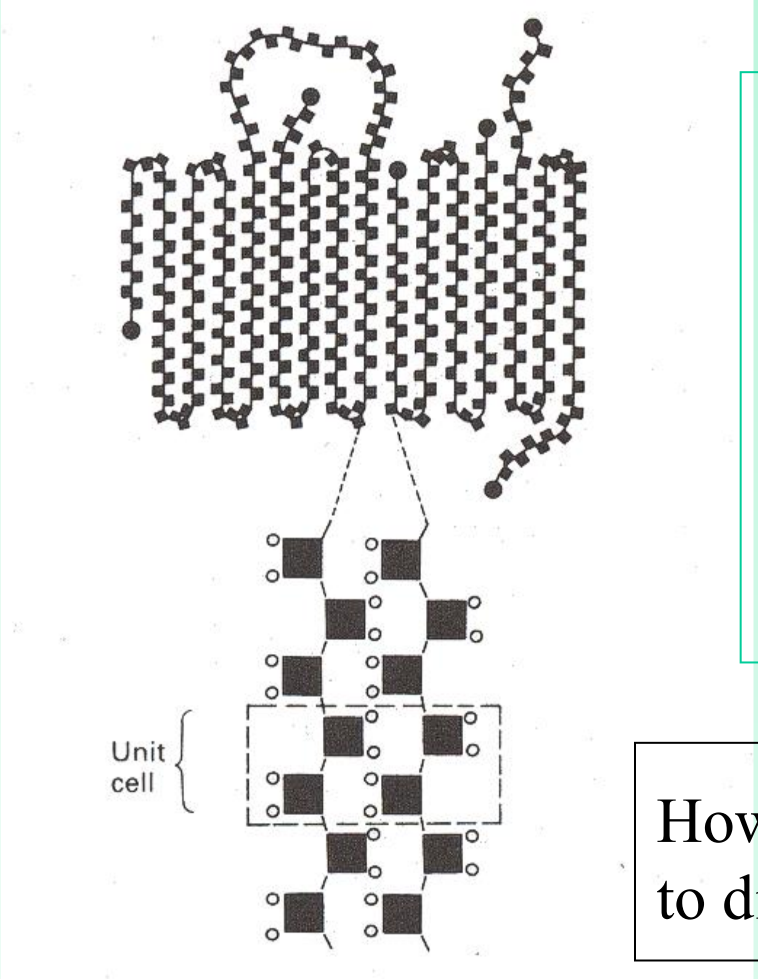
In polymers the crystalline order can be established by a regular arrangement of the chains. However, since it involves molecules (not atoms) these arrangements are much more complex.



Orthorhombic unit cell (a≠b≠c, $\alpha=\gamma=\beta=90$) of polyethylene. Note that the chain molecules extend beyond the shown unit cell

POLYMER CRYSTALLINITY (2)

High density polyethylene is an example of a crystalline polymer. Upon cooling, secondary bonds tend to pull the molecules together into parallel bundles, not perfectly crystalline but not amorphous either. Under some conditions well-defined chain-folded crystals form.

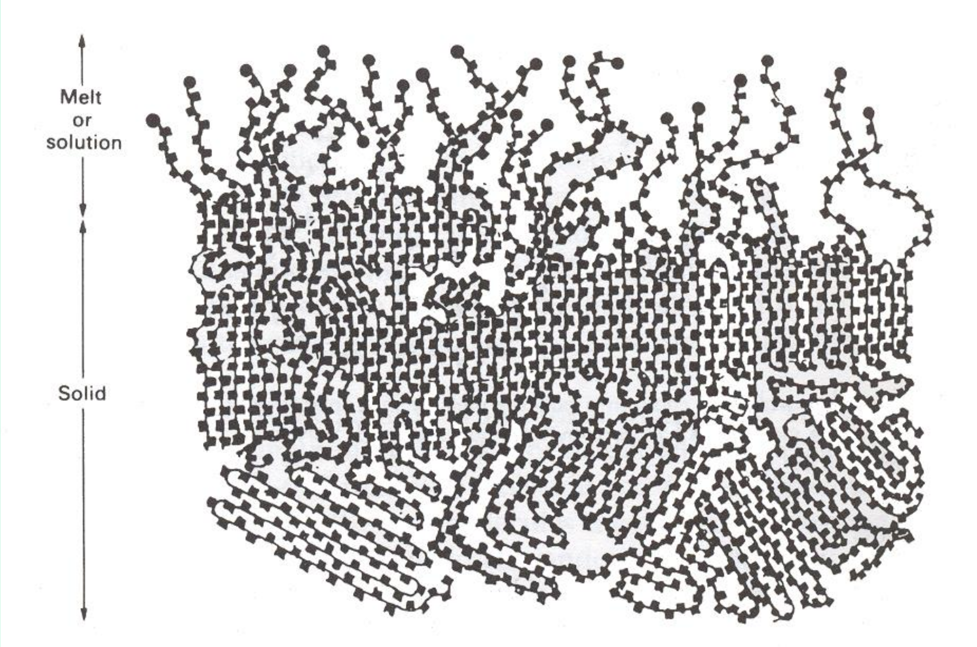


- The long molecules fold like "computer" paper into a stack with width much less than length of the molecule.
- The folds are not perfectly even, and the tails of the molecules may not tuck in properly.
- It is like a badly woven carpet!!

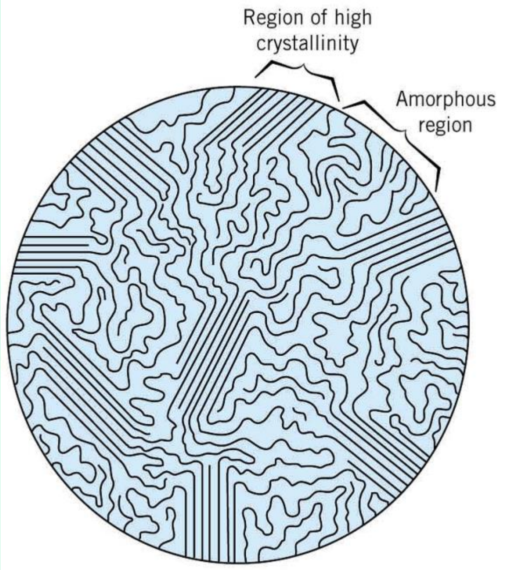
However the crystallinity is good enough to diffract X-rays like a metal crystal

POLYMER CRYSTALLINITY (3)

But even the most crystalline of polymers is only 80% crystal!!



Bundles and chain folded segments, make it largely crystalline, but these parts are separated by glassy (disordered) regions



Fringed-micelle model: small crystalline regions (micelles) in which the chains are aligned, are embedded in an amorphous matrix. A single molecule can pass through different regions.

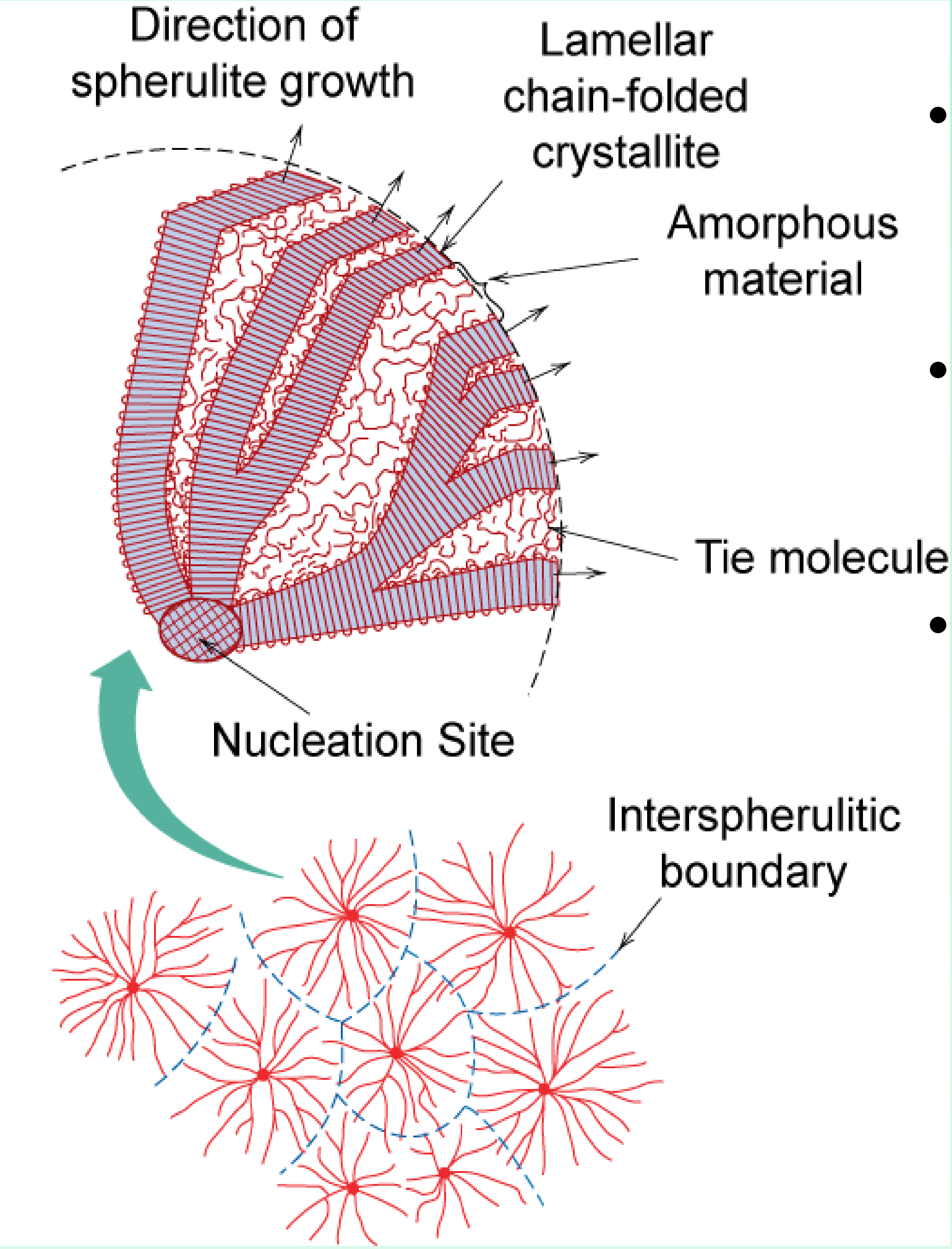
Degree of Crystallinity

Thus in polymers crystalline and amorphous regions can coexist. Disturbance of the arrangement of the long chains (twists, kinks...) results in the *local amorphization* of the polymer. Density of the amorphous phase is lower than that of the crystalline Phase. Thus density and can be used to calculate the *degree of crystallinity:*

$$\boxed{\% \text{crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \text{x}100}$$

ρ_c= density of perfect crystalline polymer
ρ_a= density of completely amorphous polymer
ρ_s= density of analyzing partially crystalline polymer

Semi-crystalline Polymers



- Some semicrystalline polymers form spherulite structures
- Alternating chain-folded crystallites and amorphous regions
- Spherulite structure for relatively rapid growth rates

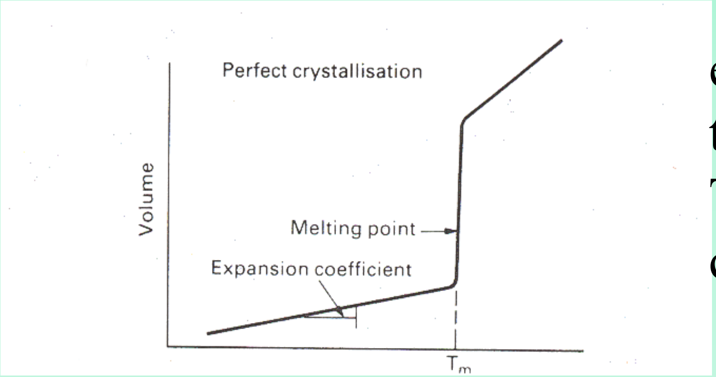
Degree of Crystallinity

Degree of crystallinity is determined by:

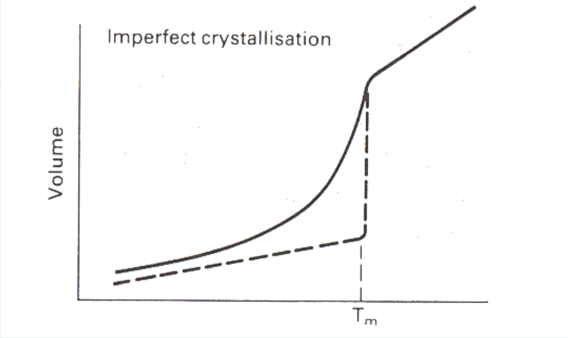
- **Rate of cooling during solidification**: time is necessary for chains to move and align into a crystal structure
- **Mer complexity**: crystallization less likely in complex structures, simple polymers, such as polyethylene, crystallize relatively easily
- **Chain configuration**: linear polymers crystallize relatively easily; branches inhibit crystallization; network polymers are almost completely amorphous; cross-linked polymers can be both crystalline and amorphous
- **Isomerism**: isotactic, syndiotactic polymers crystallize relatively easily - geometrical regularity allows chains to fit together; atactic difficult to crystallize
- **Copolymerism**: easier to crystallize if mer arrangements are more regular – alternating and block can crystallize more easily as compared to random and graft

More crystallinity: higher density, more strength, higher resistance to dissolution and softening by heating

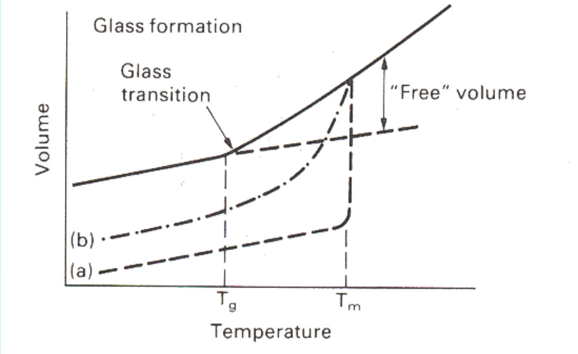
Crystallization of Different Materials



e.g. in metals, when liquid crystallizes to a solid, there is a sharp sudden decrease of volume !!
The random arrangement of the atoms in the liquid change discontinuously (same for viscosity, etc.)



Crystalline polymers behave similarly:
have a fairly well-defined melting point at which volume (a swell as viscosity) changes rapidly, blurred by the range of molecular weights



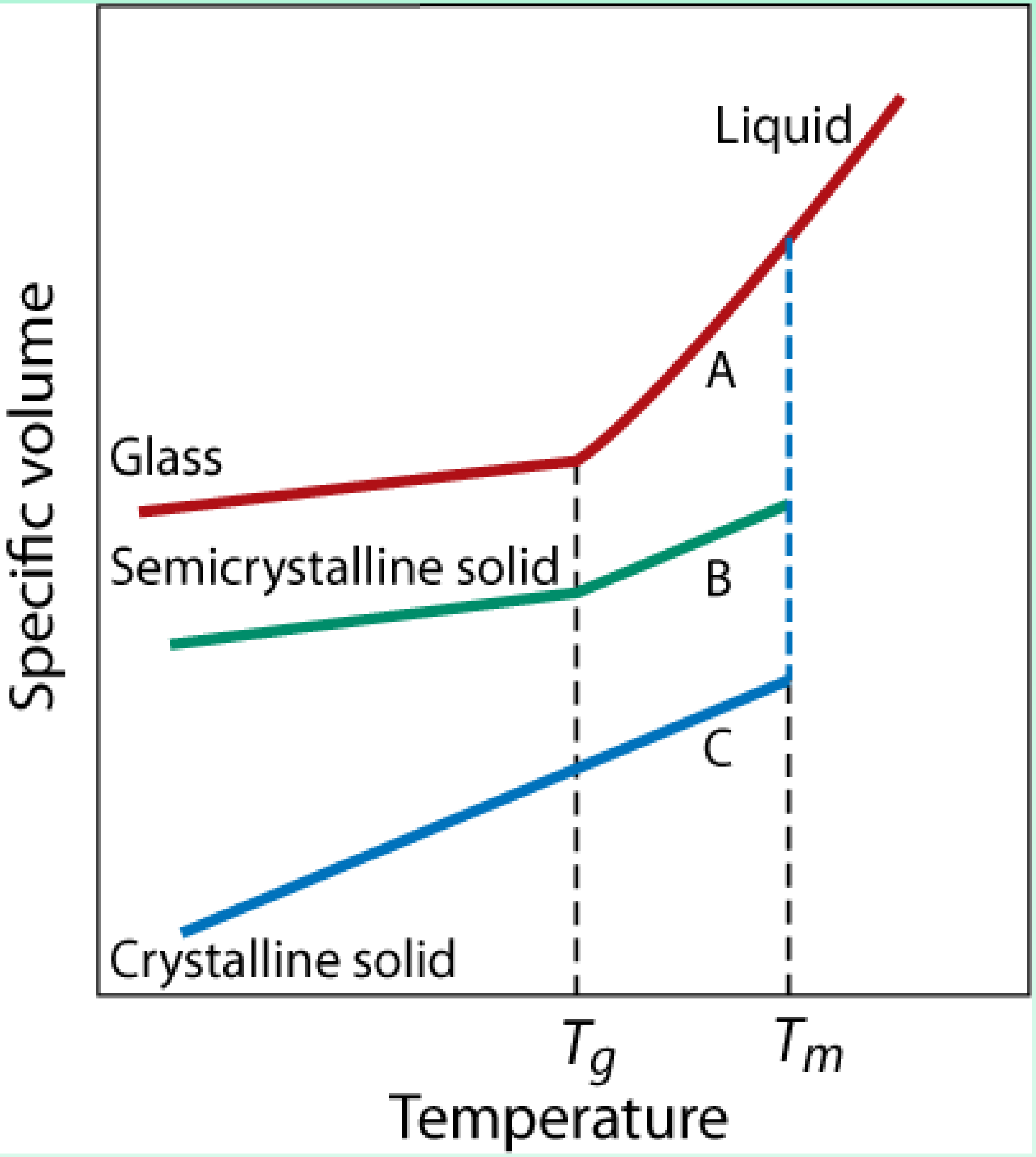
When a polymer solidified to a glass the melting point disappears completely, but new so-called glass temperature at which the free volume disappears can be defined and measured

Melting & Glass Transition Temps.

What factors affect T_m and T_g?

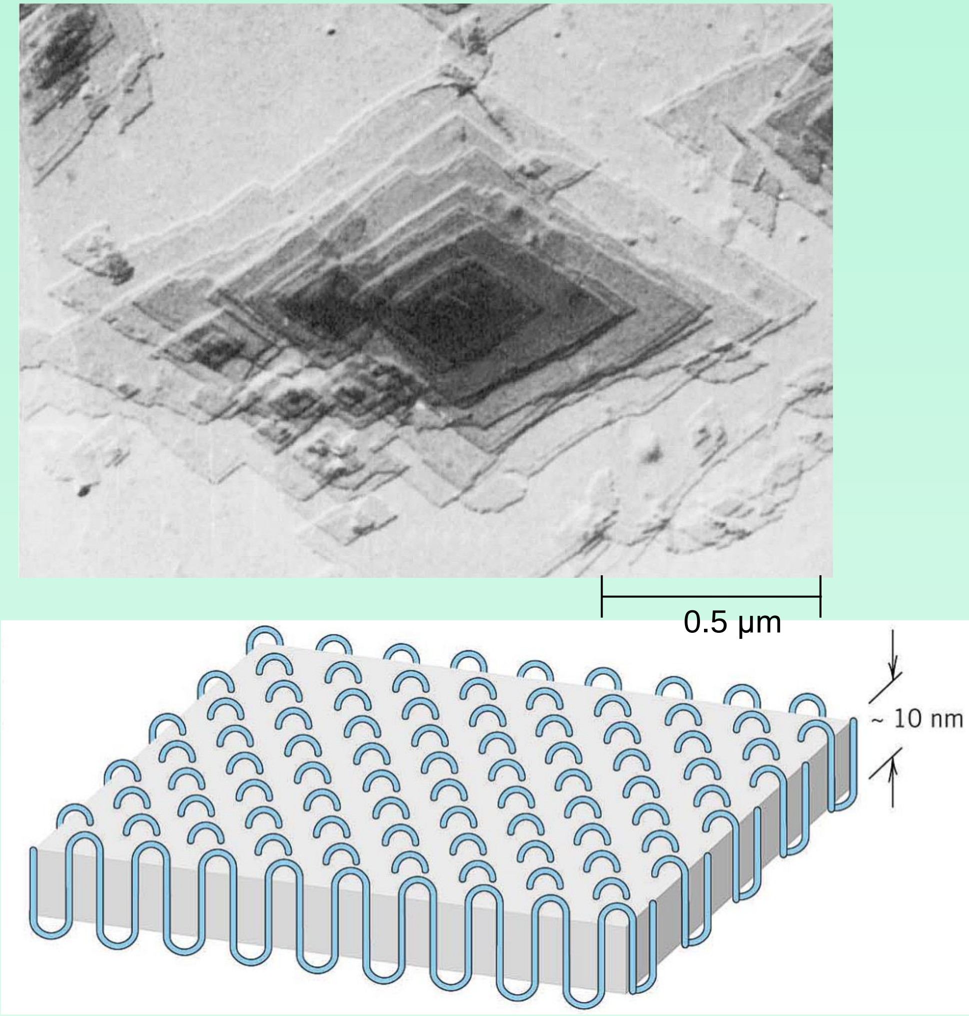
- Both T_m *and* T_g increase with increasing chain stiffness
- Chain stiffness increased by presence of
  1. Bulky side groups
  2. Polar groups or side groups
  3. Chain double bonds and aromatic chain groups

- Regularity of repeat unit arrangements – affects T_m only



Polymer Crystals

Thin crystalline platelets grown from solution. These crystals are regularly shaped thin platelets ~10 nm thick/ ~10mm long. Typically they form multilayer structures



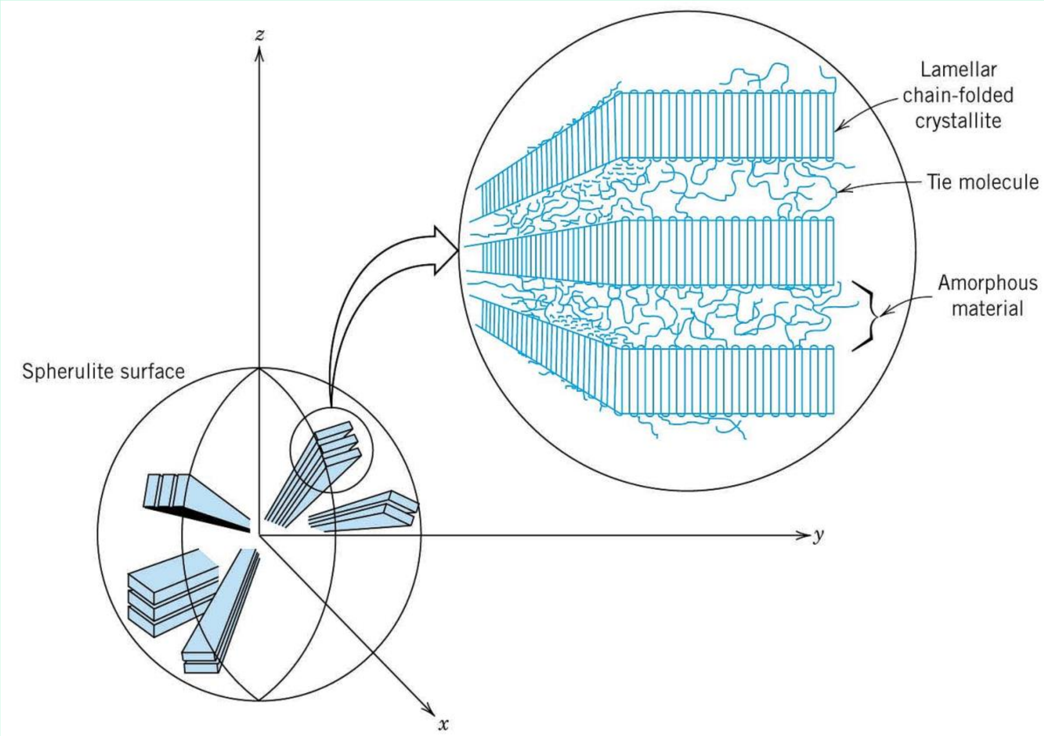
Polyethylene single crystal (TEM photo)

Single crystals – only for slow and carefully controlled growth rates

The microstructure can be described by the *chain-fold model: The* chains cross the platelet several times and are folded back and forth on themselves. The average chain length is much greater than the thickness of the crystallite

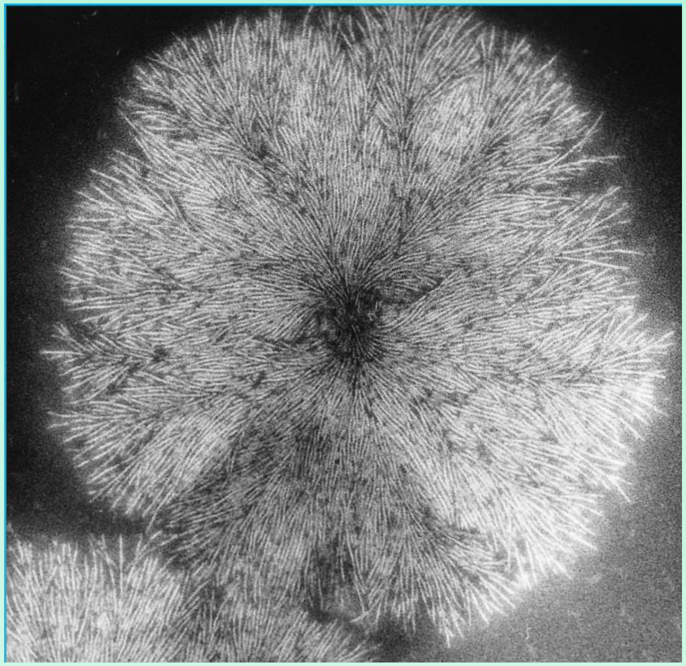
Spherulites

Often the crystalline platelets organize themself into **spherulites**;
spherical aggregates of the lamellar crystallites (~10nm thick), separated by amorphous material.

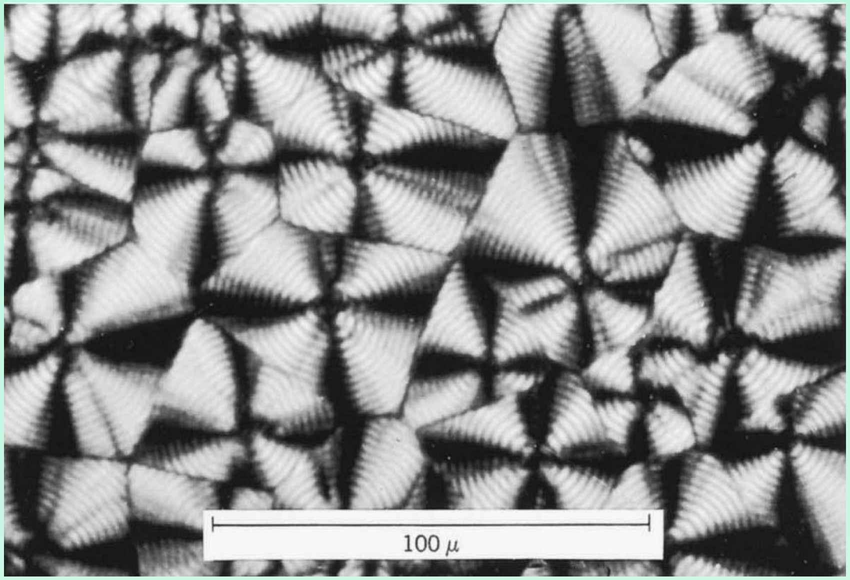


The growing ends of a small bundle crystallites trap amorphous material between them, wedging them apart. More crystallites nucleate on the bundle and they splay out as they grow. The splaying continues until the crystallites bend back on themselves and touch.

Spherulites



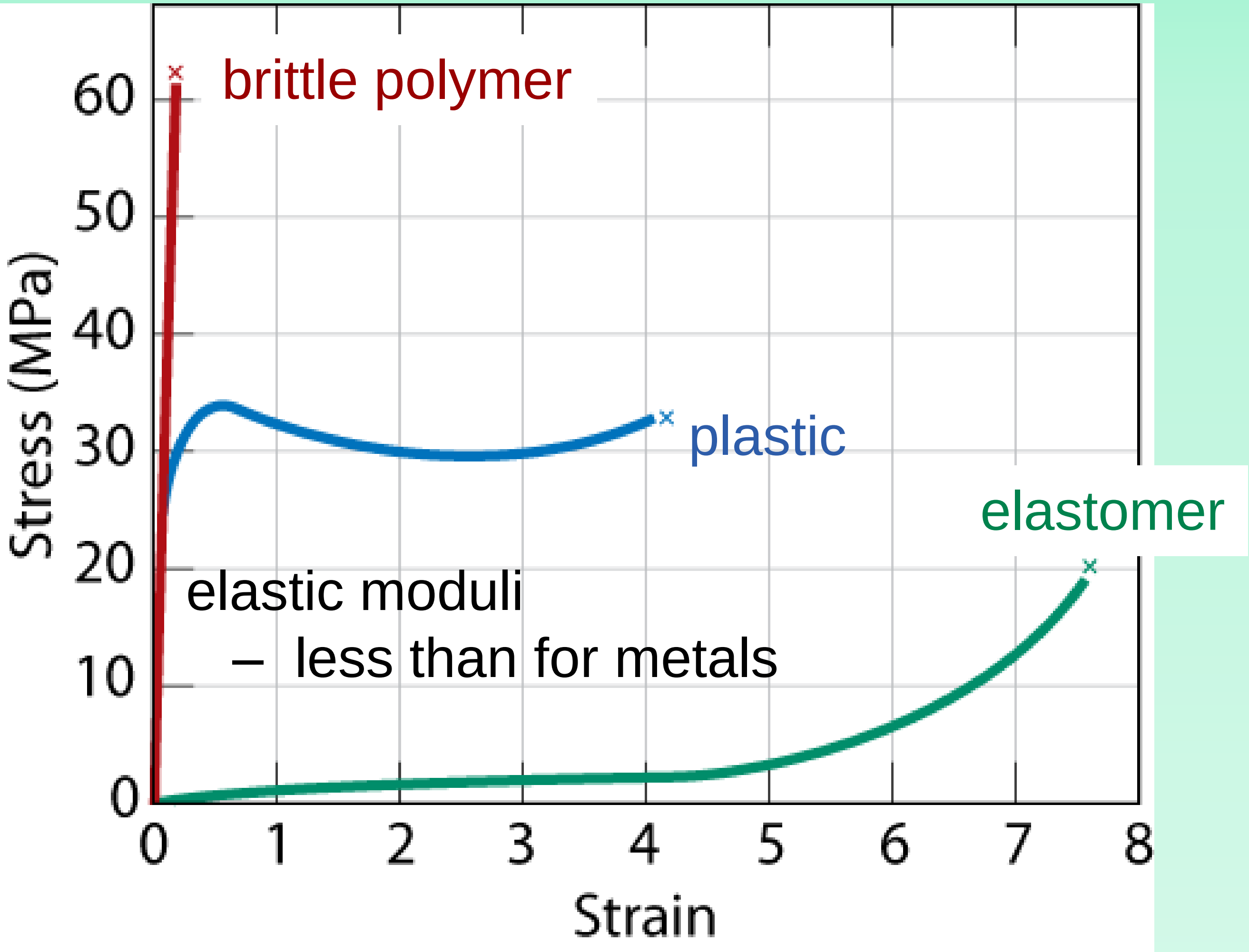
TEM micrograph of spherulite structure in natural rubber Specimen (x ~20,000).



A micrograph in cross-polarized light of spherulite structure of Polyethylene (x~ 500).

Mechanical Properties

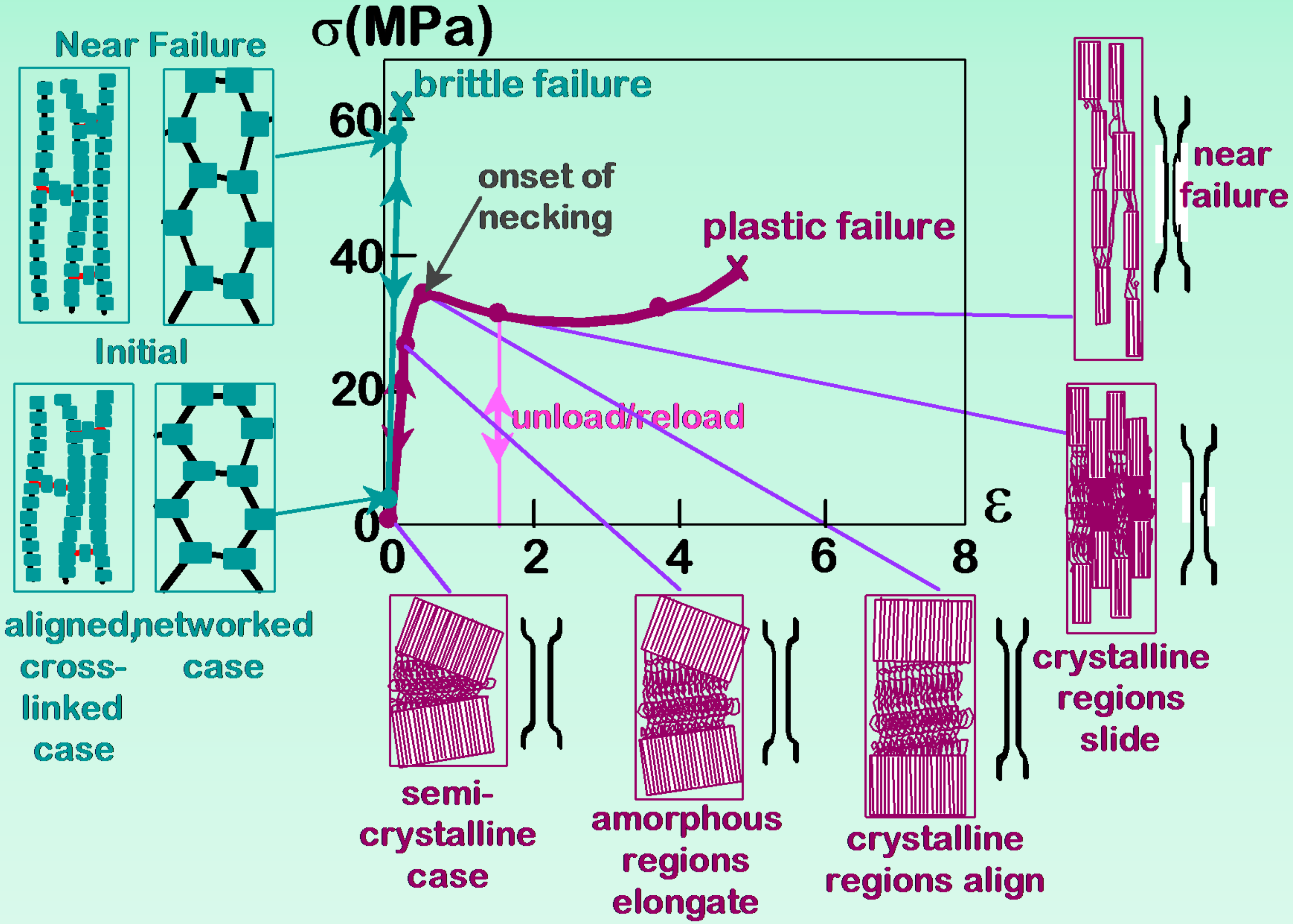
Mechanical Properties of Polymers – Stress-Strain Behavior



elastic moduli
 – less than for metals

- Fracture strengths of polymers ~ 10% of those for metals
- Deformation strains for polymers > 1000%
  - for most metals, deformation strains < 10%

TENSILE RESPONSE: BRITTLE & PLASTIC



Near Failure

Initial

aligned, cross-linked case

networked case

semi-crystalline case

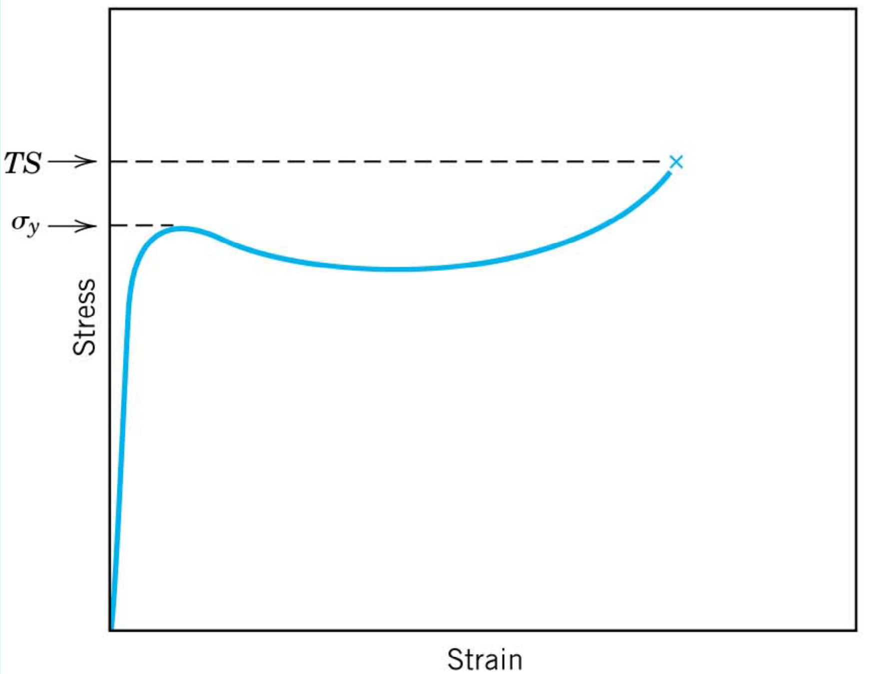
amorphous regions elongate

crystalline regions align

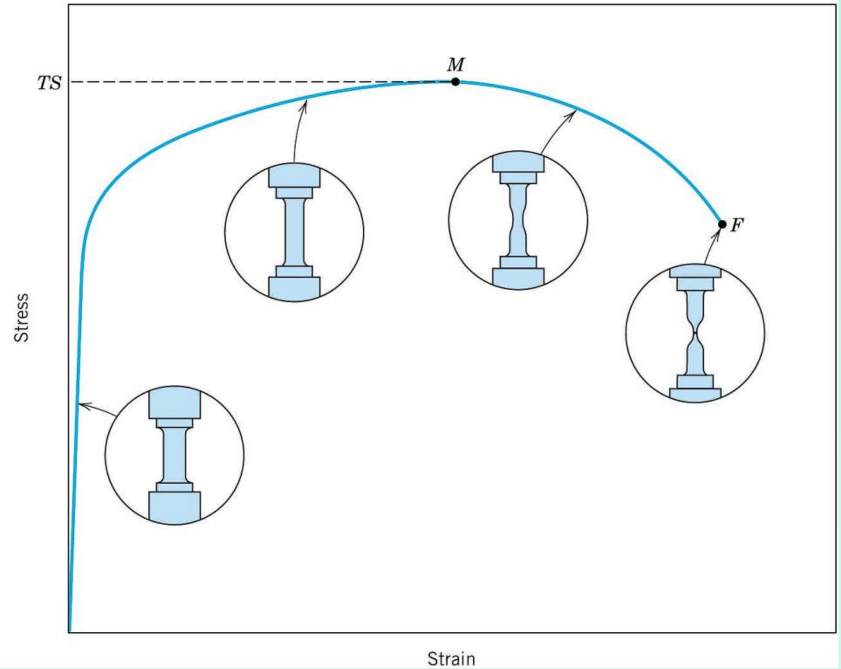
crystalline regions slide

Yield and Tensile Strength

Polymer

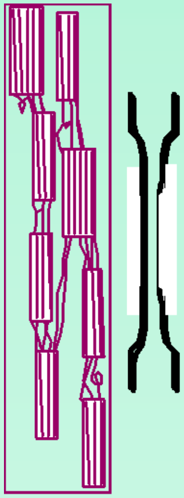


Metal

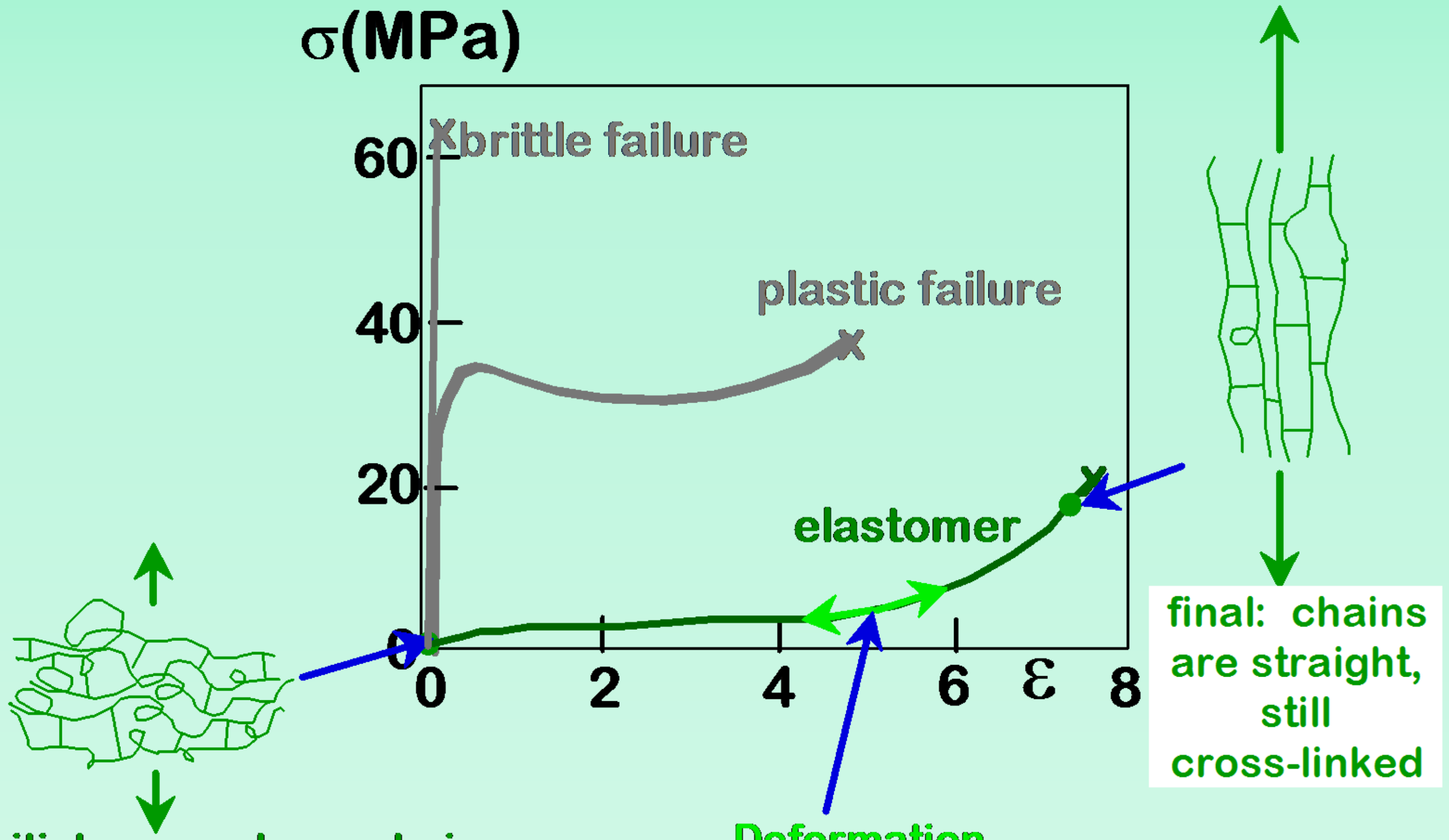


PREDEFORMATION BY DRAWING

- Drawing...
  --stretches the polymer prior to use
  --aligns chains to the stretching direction
- Results of drawing:
  --increases the elastic modulus (E) in the stretching dir.
  --increases the tensile strength (TS) in the stretching dir.
  --decreases ductility (%EL)
- Annealing after drawing...
  --decreases alignment
  --reverses effects of drawing.
- Compare to cold working in metals!



TENSILE RESPONSE: ELASTOMER CASE



final: chains are straight, still cross-linked

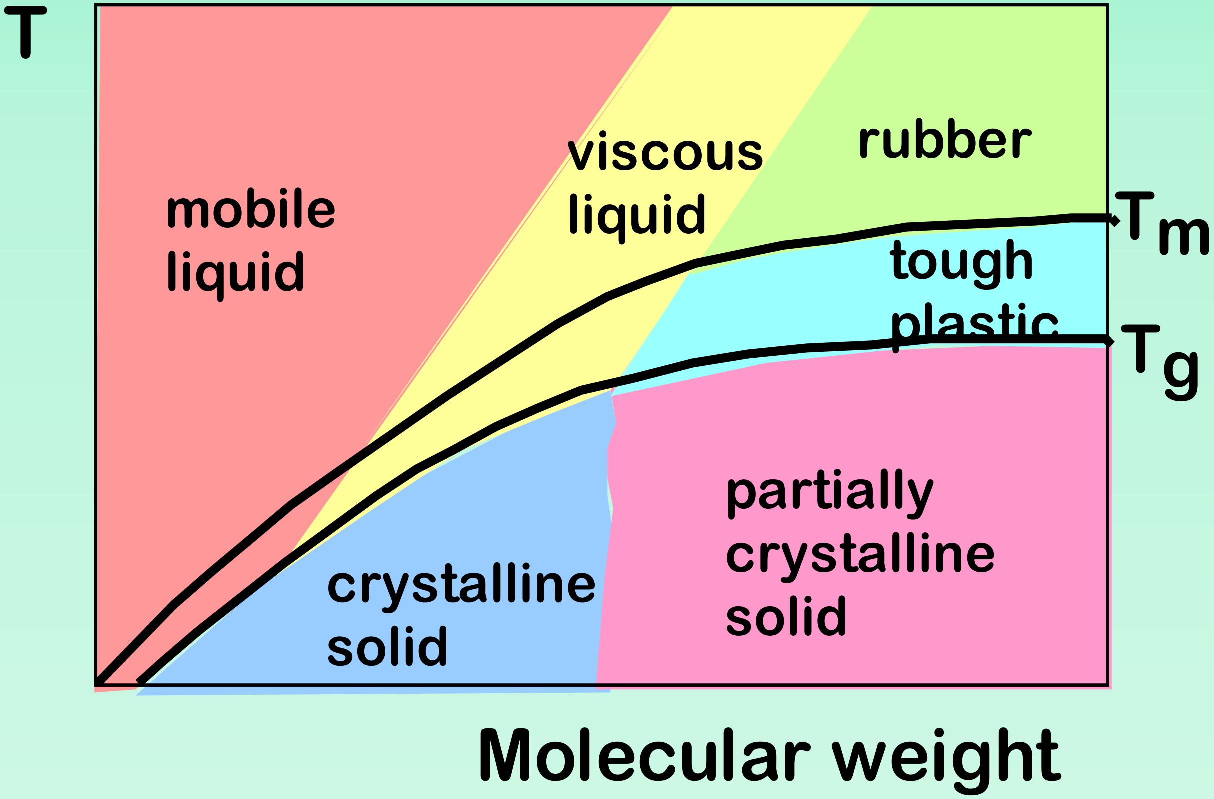
initial: amorphous chains are kinked, heavily cross-linked.

Deformation is reversible!

- Compare to responses of other polymers:
  - --brittle response (aligned, cross linked & networked case)
  - --plastic response (semi-crystalline case)

THERMOPLASTICS VS THERMOSETS

- **Thermoplastics**:
  --little cross linking
  --ductile
  --soften w/heating
  --polyethylene (#2)
  polypropylene (#5)
  polycarbonate
  polystyrene (#6)

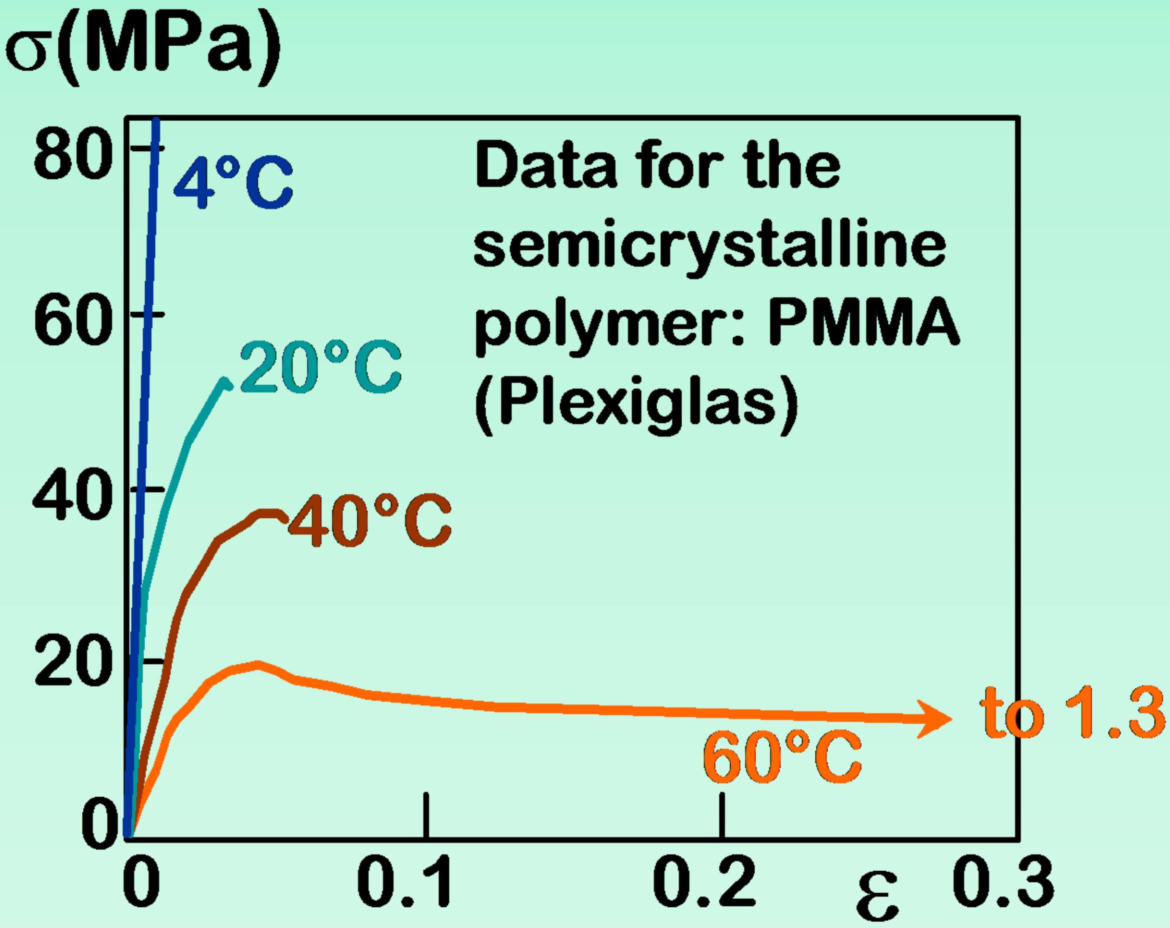


- **Thermosets**:
  --high cross linking
  (10 to 50% of mers)
  --hard and brittle
  --does NOT soften w/heating
  --vulcanized rubber, epoxies,
  polyester resin, phenolic resin

T AND STRAIN RATE: THERMOPLASTICS

- Decreasing T...
  --increases E
  --increases TS
  --decreases %EL

- Increasing strain rate...
  --same effects as decreasing T.



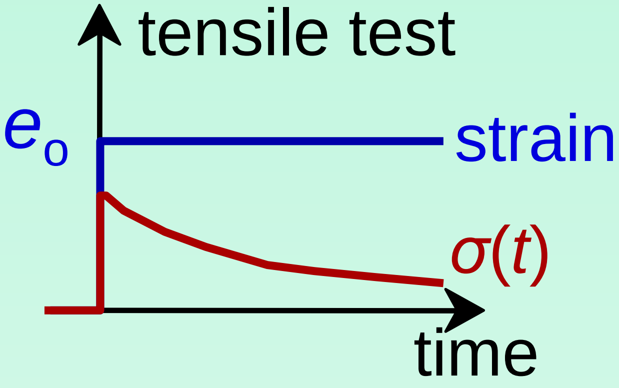
Data for the semicrystalline polymer: PMMA (Plexiglas)

Time-Dependent Deformation

- Stress relaxation test:

  -- strain in tension to e_o and hold.

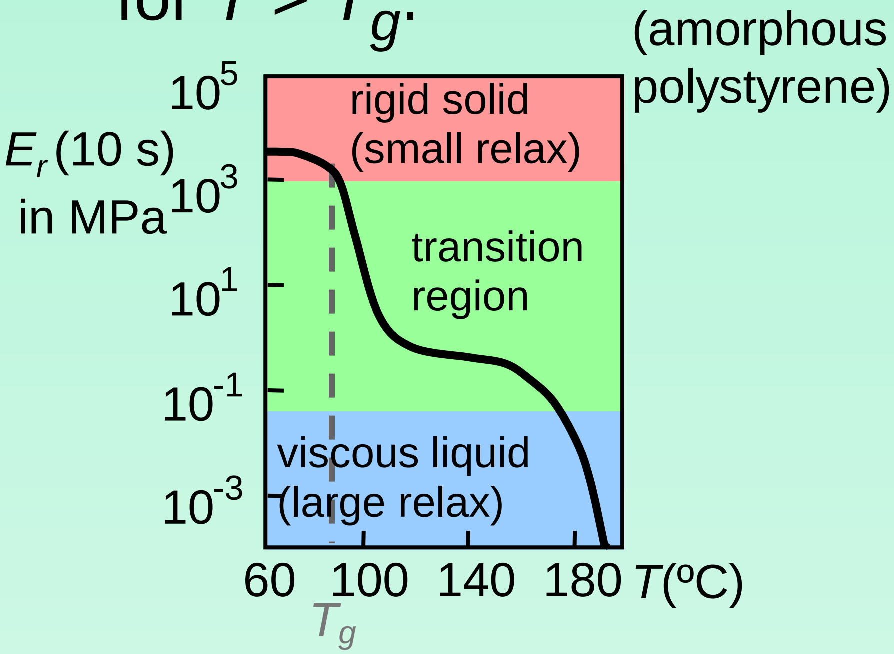
  -- observe decrease in stress with time.



- Relaxation modulus:

$$E_r(t) = \frac{\sigma(t)}{\epsilon_o}$$

- There is a large decrease in E_r for $T > T_g$.



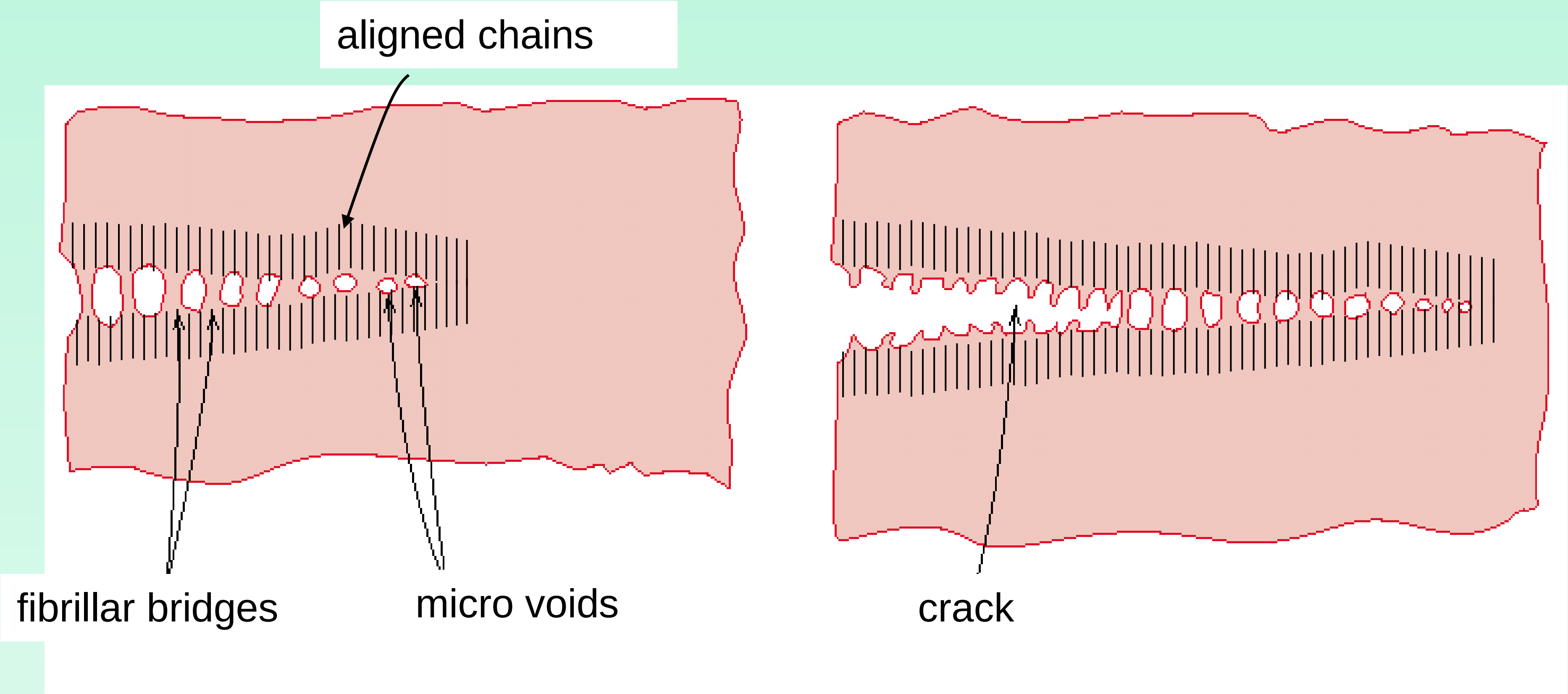
- Representative T_g values (°C):

PE (low density)	- 110
PE (high density)	- 90
PVC	+ 87
PS	+100
PC	+150

Crazing During Fracture of Thermoplastic Polymers

Craze formation prior to cracking

- during crazing, plastic deformation of spherulites
- and formation of micro voids and fibrillar bridges



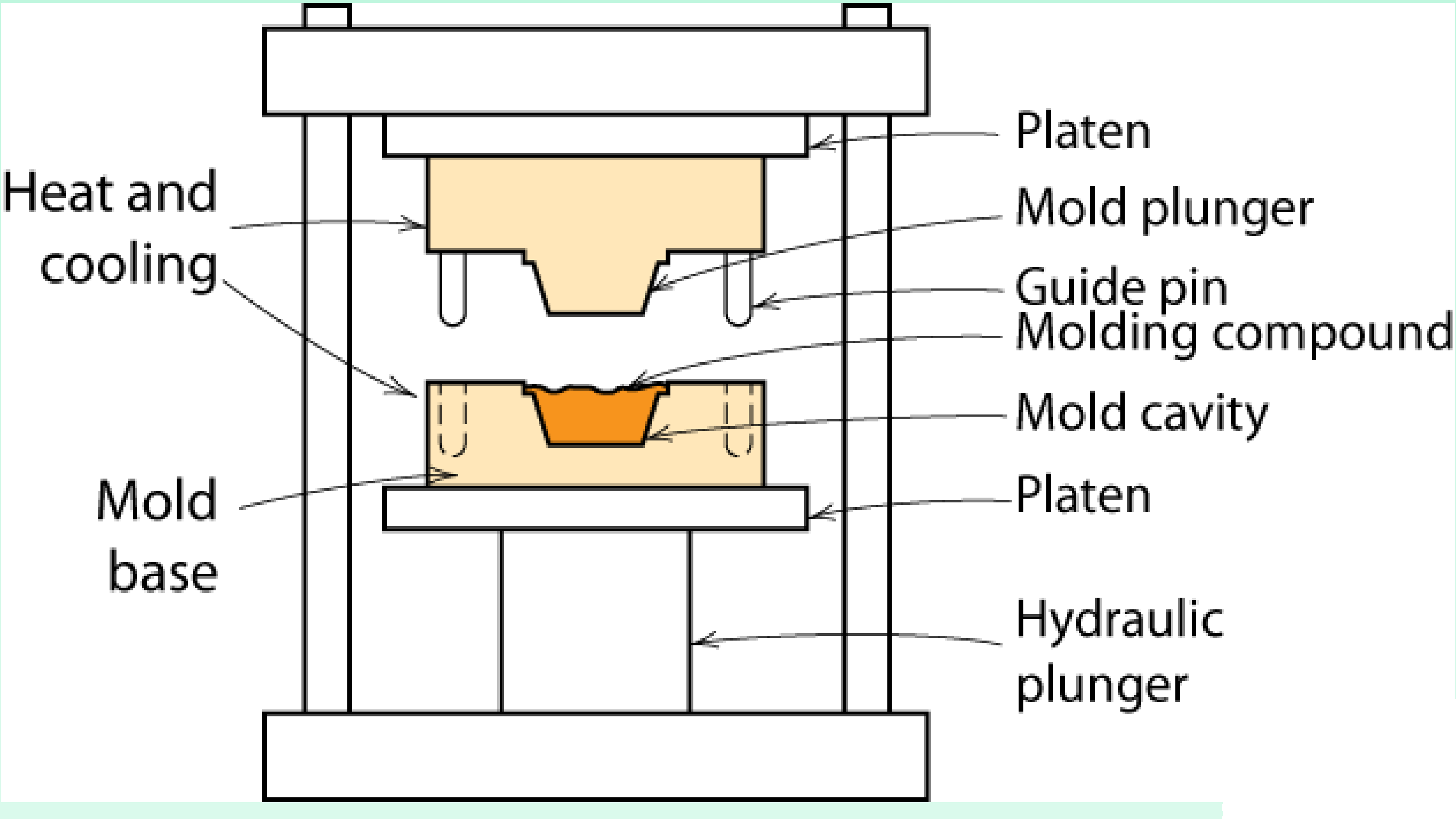
Processing of Plastics

- Thermoplastic
  - can be reversibly cooled & reheated, i.e. recycled
  - heat until soft, shape as desired, then cool
  - ex: polyethylene, polypropylene, polystyrene.
- Thermoset
  - when heated forms a molecular network (chemical reaction)
  - degrades (doesn't melt) when heated
  - a prepolymer molded into desired shape, then chemical reaction occurs
  - ex: urethane, epoxy

Processing Plastics – Compression Molding

Thermoplastics and thermosets

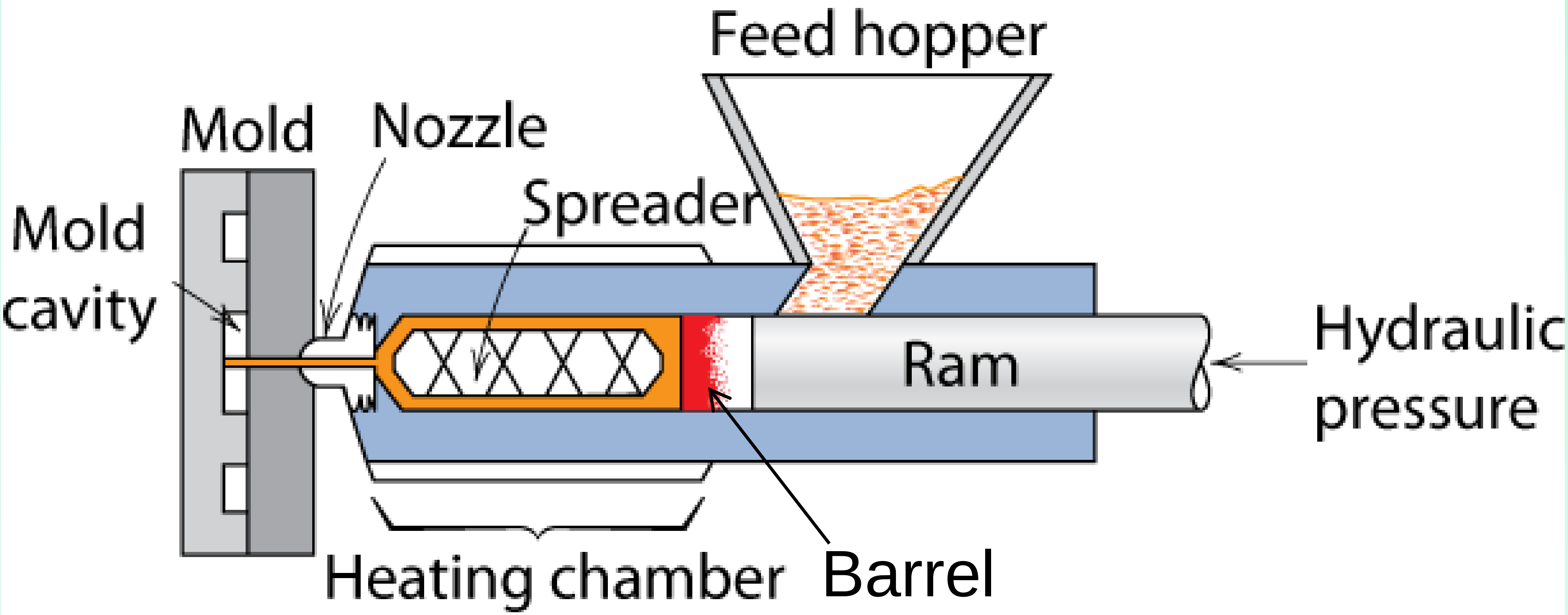
- polymer and additives placed in mold cavity
- mold heated and pressure applied
- fluid polymer assumes shape of mold



Processing Plastics – Injection Molding

Thermoplastics and some thermosets

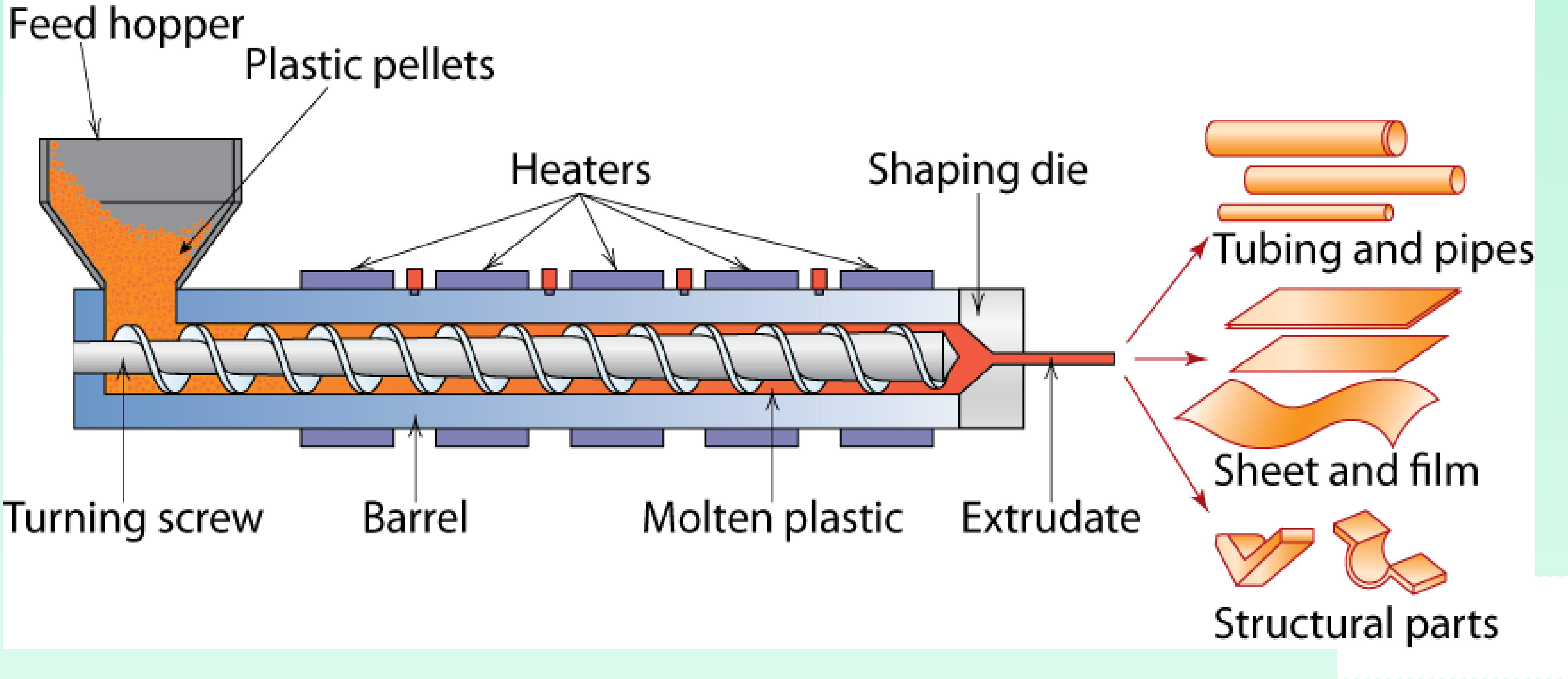
- when ram retracts, plastic pellets drop from hopper into barrel
- ram forces plastic into the heating chamber (around the spreader) where the plastic melts as it moves forward
- molten plastic is forced under pressure (injected) into the mold cavity where it assumes the shape of the mold



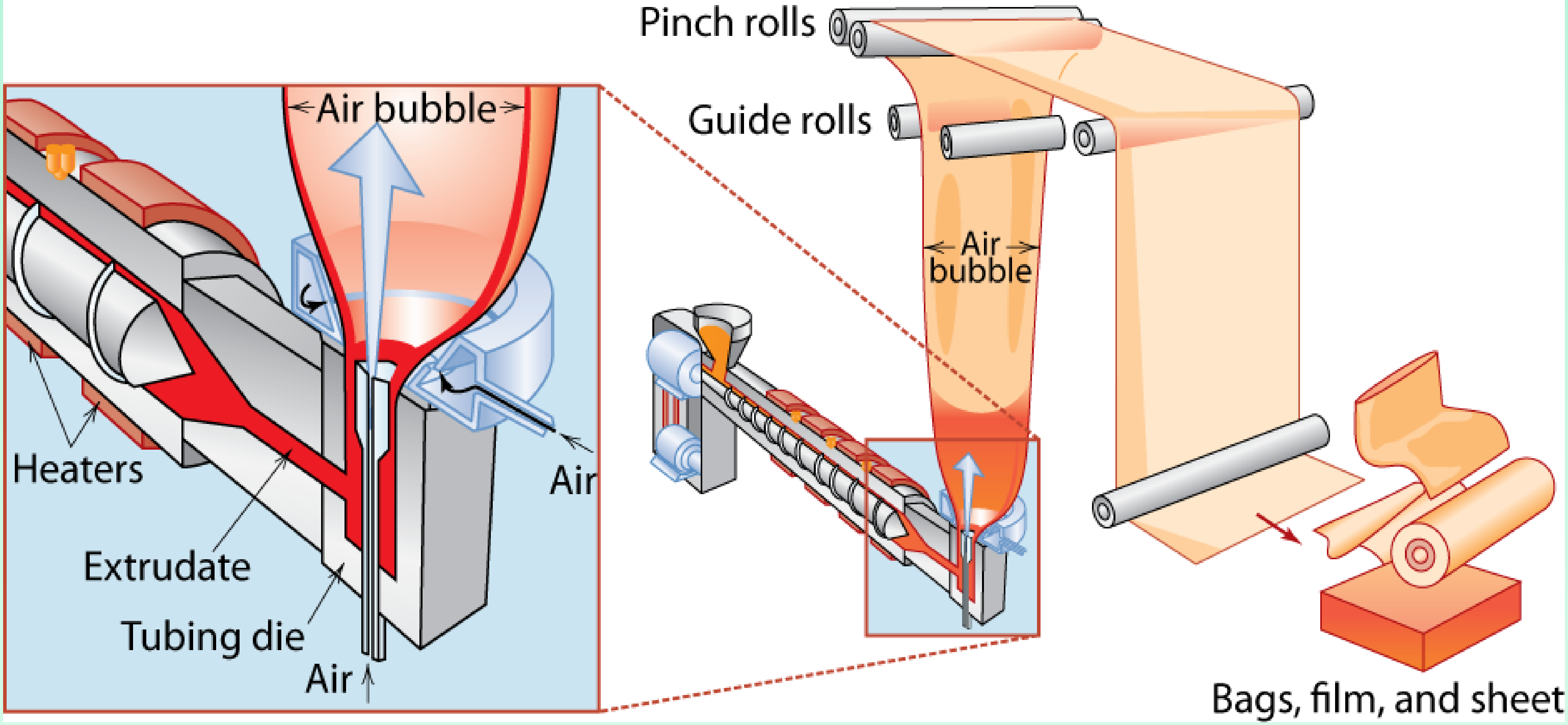
Processing Plastics – Extrusion

thermoplastics

- plastic pellets drop from hopper onto the turning screw
- plastic pellets melt as the turning screw pushes them forward by the heaters
- molten polymer is forced under pressure through the shaping die to form the final product



Processing Plastics – Blown-Film Extrusion



Polymer Types – Fibers

Fibers - length/diameter >100

- Primary use is in textiles.
- Fiber characteristics:
  - high tensile strengths
  - high degrees of crystallinity
  - structures containing polar groups
- Formed by spinning
  - extrude polymer through a spinneret (a die containing many small orifices)
  - the spun fibers are drawn under tension
  - leads to highly aligned chains - fibrillar structure

Polymer Types – Miscellaneous

- Coatings – thin polymer films applied to surfaces – i.e., paints, varnishes
  - protects from corrosion/degradation
  - decorative – improves appearance
  - can provide electrical insulation
- Adhesives – bonds two solid materials
- bonding types:
  1. Secondary – van der Waals forces
  2. Mechanical – penetration into pores/crevices
- Films – produced by blown film extrusion
- Foams – gas bubbles incorporated into plastic

Advanced Polymers

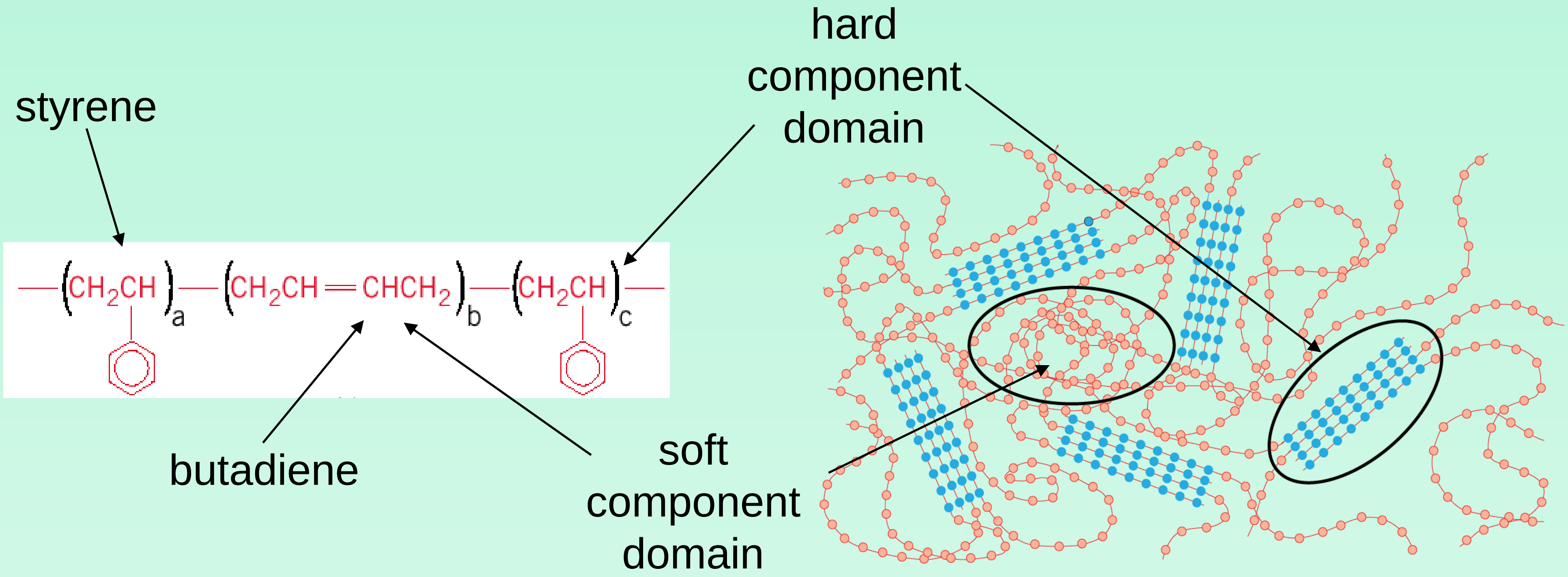
Ultrahigh Molecular Weight Polyethylene (UHMWPE)

- Molecular weight ca. 4×10^6 g/mol
- Outstanding properties
  - high impact strength
  - resistance to wear/abrasion
  - low coefficient of friction
  - self-lubricating surface
- Important applications
  - bullet-proof vests
  - golf ball covers
  - hip implants (acetabular cup)

Advanced Polymers

Thermoplastic Elastomers

Styrene-butadiene block copolymer



$$-\left(CH_2CH\right)_a-\left(CH_2CH{=}CHCH_2\right)_b-\left(CH_2CH\right)_c-$$

styrene

butadiene

hard
component
domain

soft
component
domain

Summary

- Limitations of polymers:
  - -- E, σ_y, K_c, $T_{\text{application}}$ are generally small.
  - -- Deformation is often time and temperature dependent.
- Thermoplastics (PE, PS, PP, PC):
  - -- Smaller E, σ_y, $T_{\text{application}}$
  - -- Larger K_c
  - -- Easier to form and recycle
- Elastomers (rubber):
  - -- Large reversible strains!
- Thermosets (epoxies, polyesters):
  - -- Larger E, σ_y, $T_{\text{application}}$
  - -- Smaller K_c

Table 15.3 *Callister & Rethwisch 9e*:

Good overview of applications and trade names of polymers.

Summary

- Polymer Processing
  -- compression and injection molding, extrusion, blown film extrusion
- Polymer melting and glass transition temperatures
- Polymer applications
  -- elastomers
  -- fibers
  -- coatings
  -- adhesives
  -- films
  -- foams
  -- advanced polymeric materials