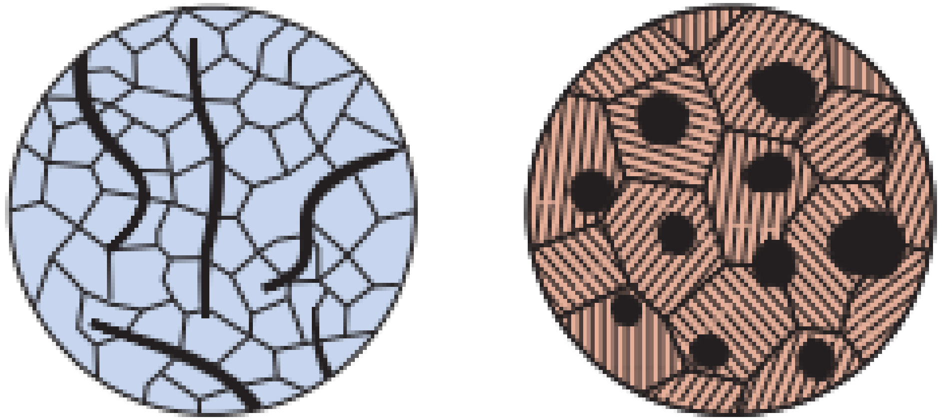
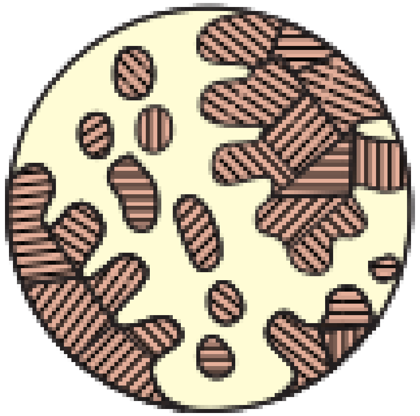
Recap

- Understood Ferrous and Non-Ferrous alloys (Taxonomy).
- Identified steels and cast irons based on carbon content and microstructure.
- Identified plain and heat treatable low alloy steels.
- Identified three types of stainless steels and their characteristics.
- Saw briefly the grading of steels provided by ASMT/AISI/SAE.
- Graphitization in cast irons.
- Four classifications of cast iron.
- Classified based on shape of graphite.
- Matrix was pearlite or ferrite based on cooling rate.
- Limitations of ferrous and other alloys.

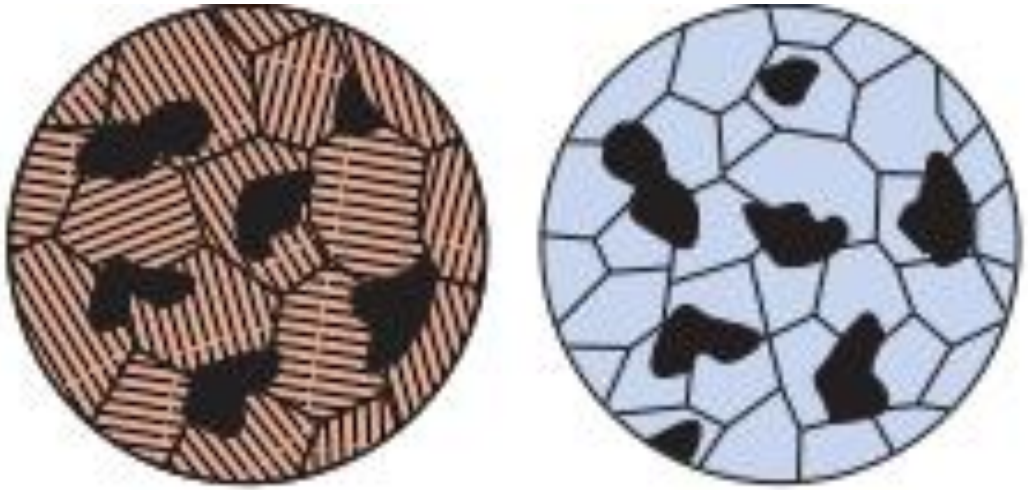
Test your retention



Ferritic gray cast iron, pearlitic ductile cast iron



White cast iron



Pearlitic malleable, Ferritic malleable

1. What elements are added to plain carbon steels to make them heat treatable?
2. What is the Chromium content in stainless steels?
3. What is the element and its content required for Graphitization?

Topics to be covered this week

Polymers – types of polymers, molecular weight, calculation of molecular weight examples, importance of molecular weight, Polymers – amorphous and crystalline polymers, Processing of polymers.
Polymers – amorphous and crystalline polymers, stress strain curves for polymers and rubbers, Creep, Stress relaxation, Glass transition temperature. Advanced polymers – UHMWPE, thermoplastic elastomers, liquid crystal polymers, Applications of polymers and their applications in various fields
Ceramics – types of ceramics and their important properties, glass transition temperature and viscosity; Heat treatment of ceramics – annealing and tempering, Processing of ceramic
Composite materials – introduction and classification of composites, properties and applications of PMCs, CMCs, and MMCs – Case study on application of composites. Processing of composite products; Nanocomposites – types of nanomaterials, properties and applications in various fields

Polymers

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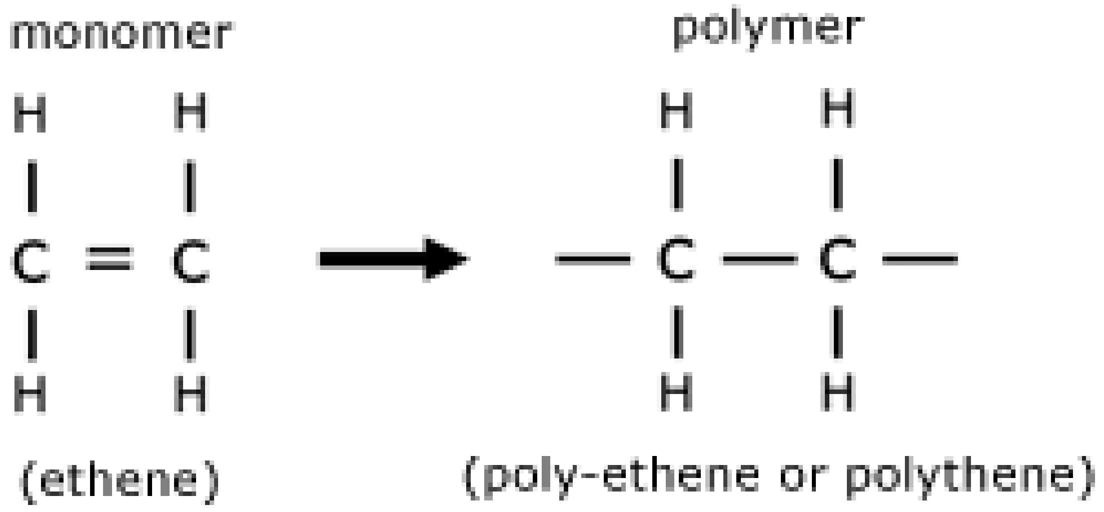
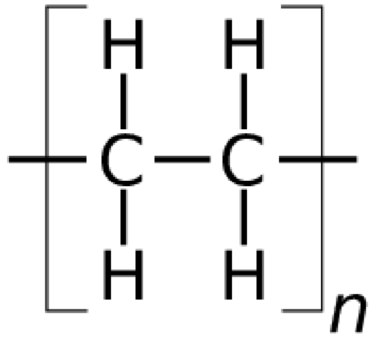
Polymers

Polymers are large macromolecules formed by joining a large number of smaller units called <u>monomers</u> through covalent chemical bonds



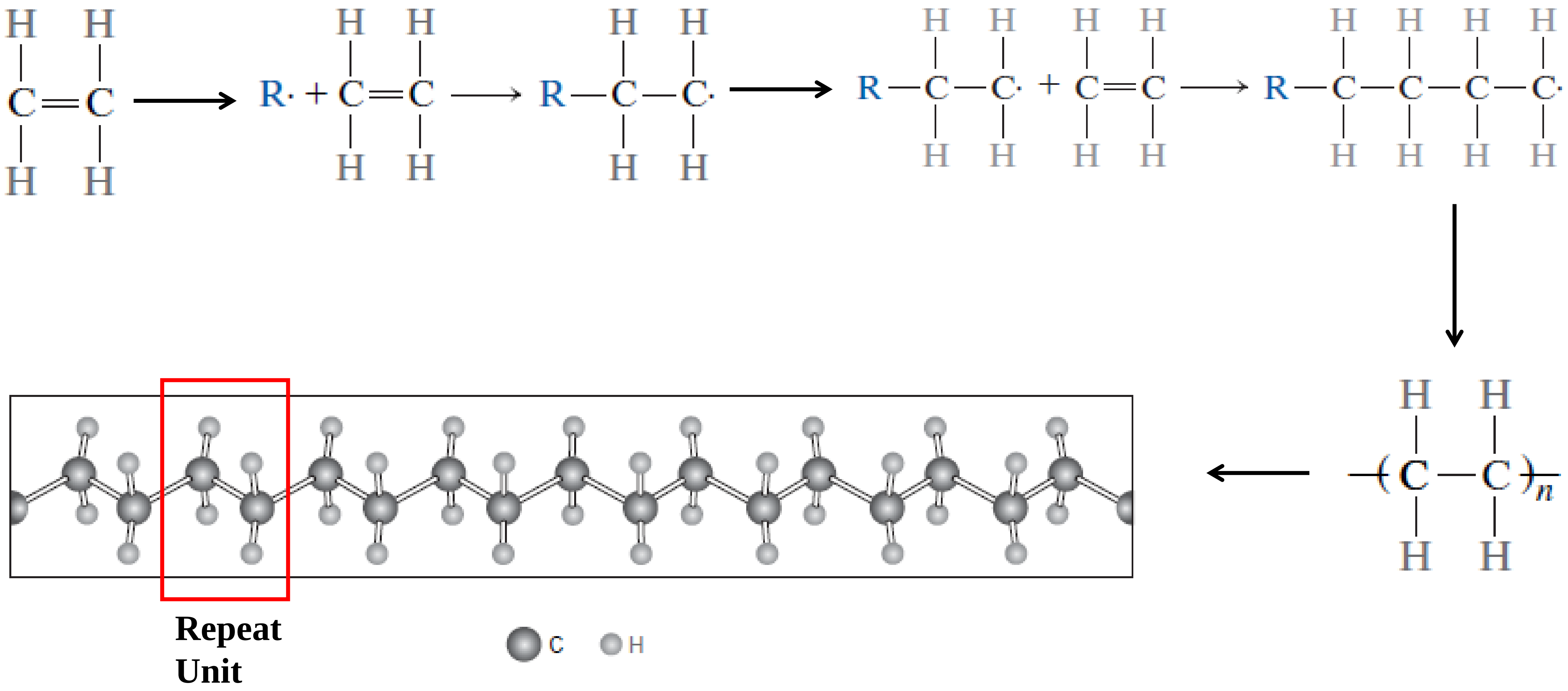


- Naturally occurring polymers – wood, rubber, cotton, wool, leather and silk, proteins, DNA/RNA, enzymes, starches and cellulose.

- Synthetic polymers - Teflon, Nylon, Polyethene, PVC, Polycarbonate etc.,

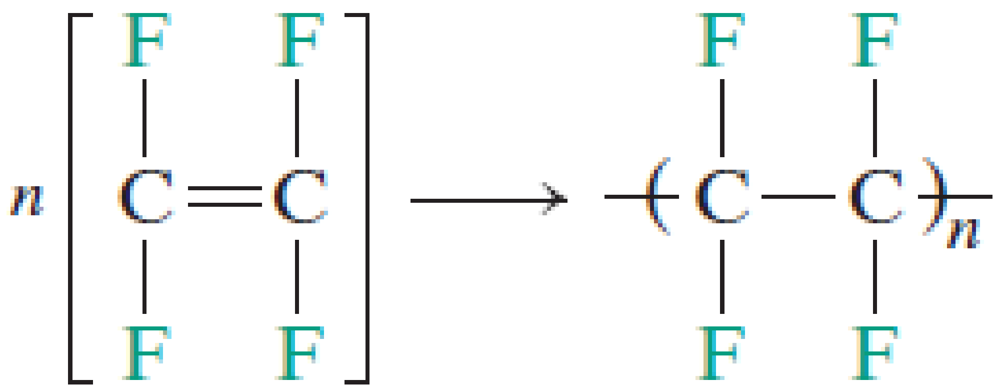
Polymer molecules – Chemistry

Polyethylene, a solid material from ethylene, which is gaseous state under room temperature and pressure.

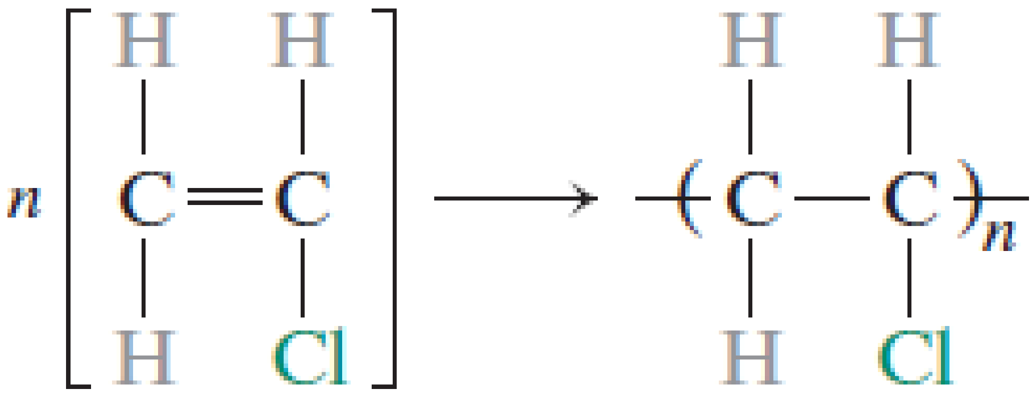


Polymer molecules – Chemistry

Polytetrafluroethylene (PTFE) a fluorocarbon, is hydrophobic.



Polyvinylchloride (PVC)



Polymer molecules – Chemistry

- When all the repeating units are same, polymers are called **homopolymers**.

- Two or more repeat units result in formation of **copolymers**. **Block, Alternating** and **Random copolymers** are the types within this category.

—A—B—A—B—A—B—A—B—A—B—A—B—A—B—

alternating copolymer

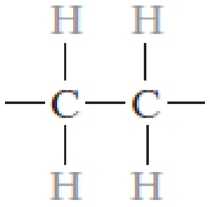
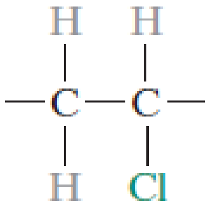
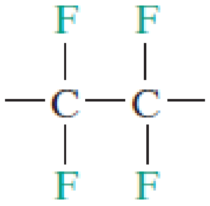
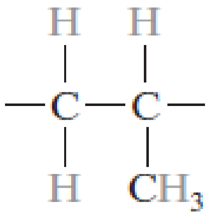
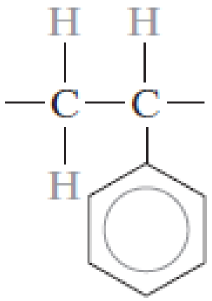
—A—A—B—A—B—B—A—B—A—A—B—B—B—A—

random copolymer

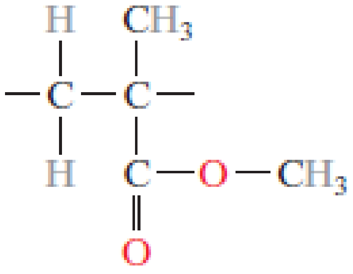
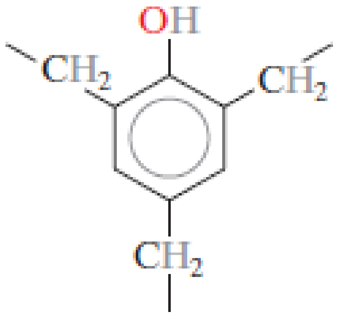
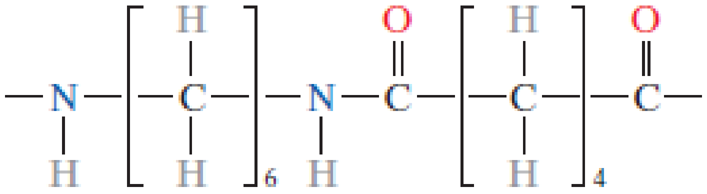
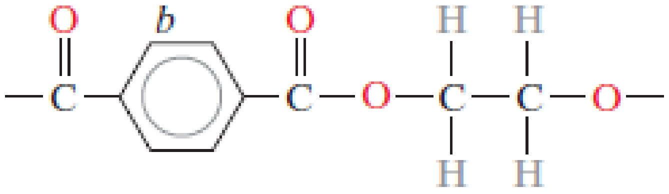
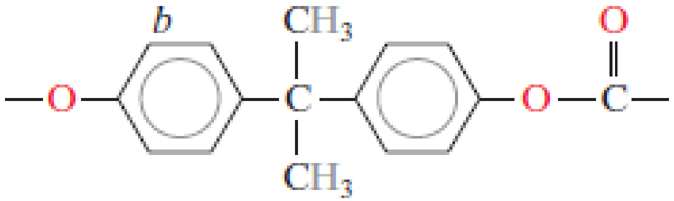
—A—A—A—A—A—A—A—B—B—B—B—B—B—B—

block copolymer

Polymer molecules – Chemistry

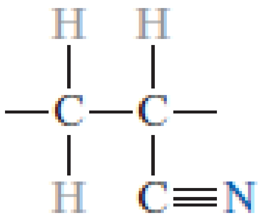
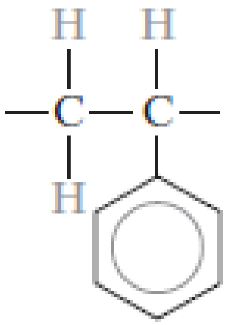
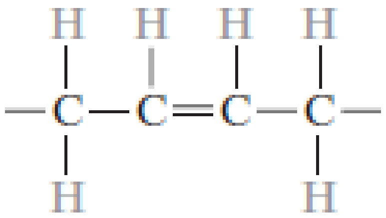
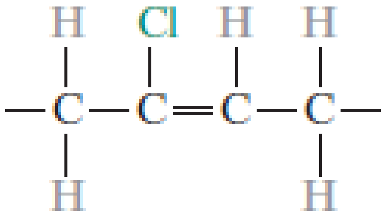
Polymer	*Repeat Unit*
Polyethylene (PE)	
Poly(vinyl chloride) (PVC)	
Polytetrafluoroethylene (PTFE)	
Polypropylene (PP)	
Polystyrene (PS)	

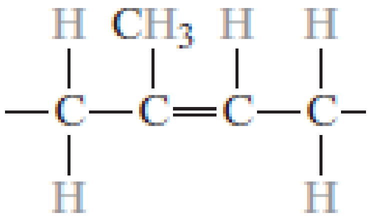
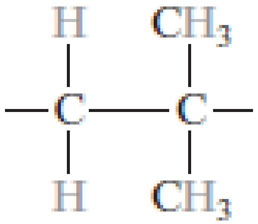
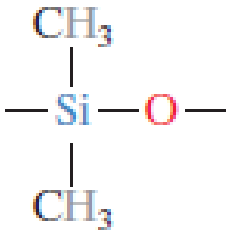
Polymer molecules – Chemistry

Polymer	*Repeat Unit*
Poly(methyl methacrylate) (PMMA)	
Phenol-formaldehyde (Bakelite)	
Poly(hexamethylene adipamide) (nylon 6,6)	
Poly(ethylene terephthalate) (PET, a polyester)	
Polycarbonate (PC)	

Polymer molecules – Chemistry

Repeat units for various copolymer rubbers

Repeat Unit Name	*Repeat Unit Structure*
Acrylonitrile	
Styrene	
Butadiene	
Chloroprene	

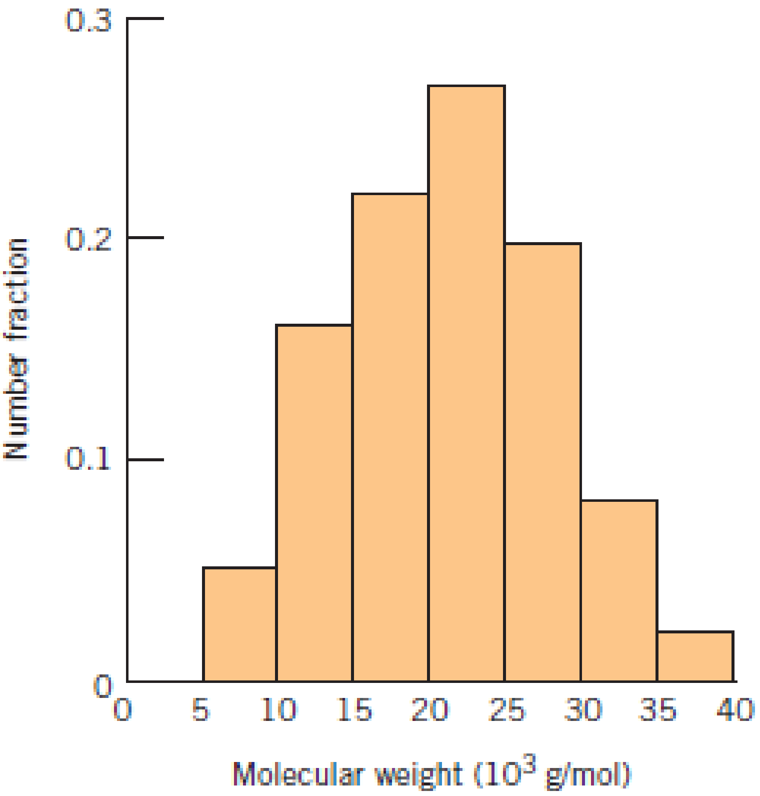
Repeat Unit Name	*Repeat Unit Structure*
Isoprene	
Isobutylene	
Dimethylsiloxane	

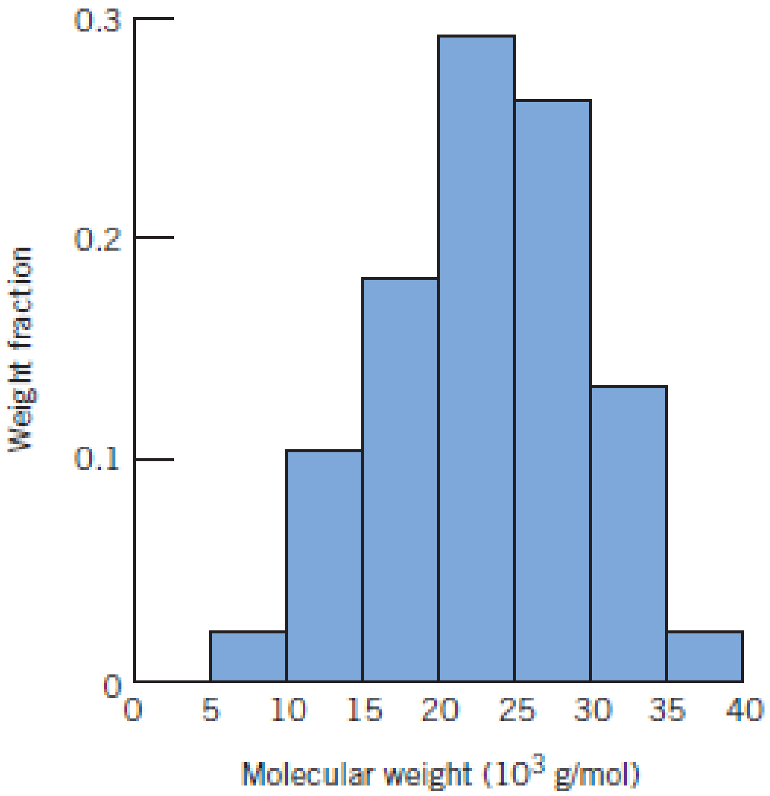
Concept of Molecular Weight of Polymers

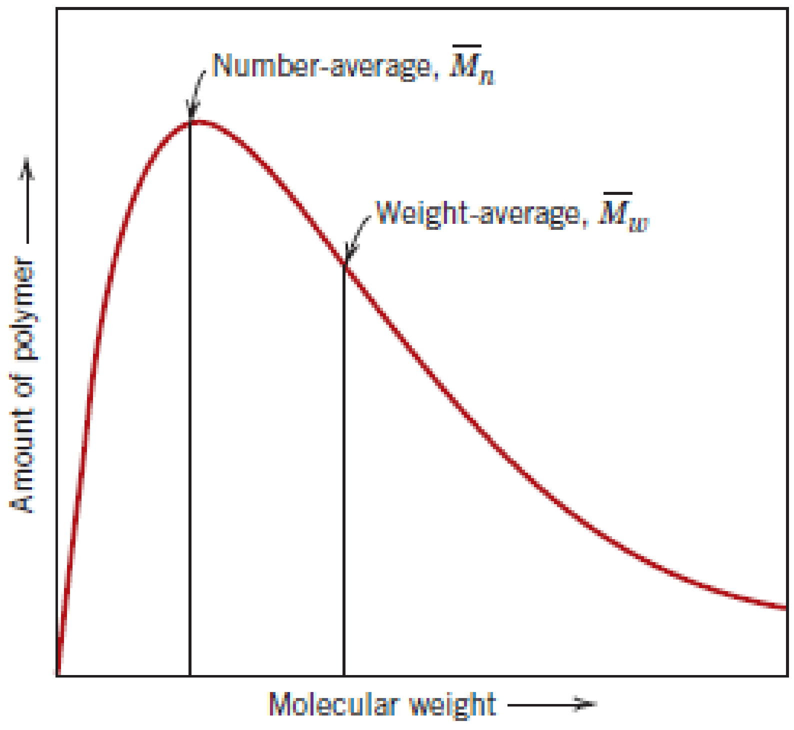
- Average molecular weight is specified.

- Number average molecular weight = $\sum_{i=1}^{N} x_i M_i$ where, x_i is the number fraction of molecules with molecular weight M_i.

- Weight average molecular weight = $\sum_{i=1}^{N} m_i M_i$ where, m_i is the weight fraction of molecules with molecular weight M_i.







Importance of Molecular Weight of Polymers

- Degree of polymerization = $\frac{\bar{M}_n}{m}$,

where, *m* the molecular weight of the repeat unit,
$\bar{M}_n$ is the average molecular weight of the polymer

- Polymer properties are strongly dependent on degree of polymerization/average chain length.

- The melting or softening temperature increases with increasing molecular weight.

1. *At room temperature, polymers with very short chains (molecular weights of 100 g/mol) will generally exist as liquids.*
2. *Molecular weights of approximately 1000 g/mol are waxy solids (such as paraffin wax) and soft resins.*
3. *Solid polymers between 10,000 and several million g/mol.*
4. *Thus, the same polymer material can have quite different properties*
5. *if it is produced with a different molecular weight.*

Computations of Average Molecular Weights and Degree of Polymerization

Assume that the molecular weight distributions shown in below are for poly(vinyl chloride). For this material, compute the following

(a) the number-average molecular weight,

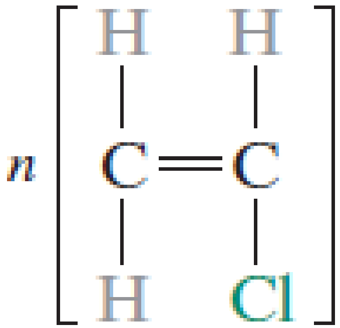
(b) the degree of polymerization, and

(c) the weight-average molecular weight.

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
			$\overline{M}_n = 21{,}150$

b) Degree of polymerization = $\frac{\bar{M}_n}{m}$,

Molecular weight of poly(vinyl chloride)



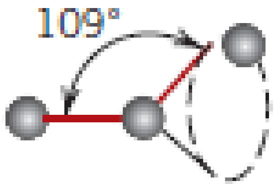
$$m = 2(12.01 \text{ g/mol}) + 3(1.01 \text{ g/mol}) + 35.45 \text{ g/mol}$$
$$= 62.50 \text{ g/mol}$$

$$DP = \frac{\overline{M}_n}{m} = \frac{21{,}150 \text{ g/mol}}{62.50 \text{ g/mol}} = 338$$

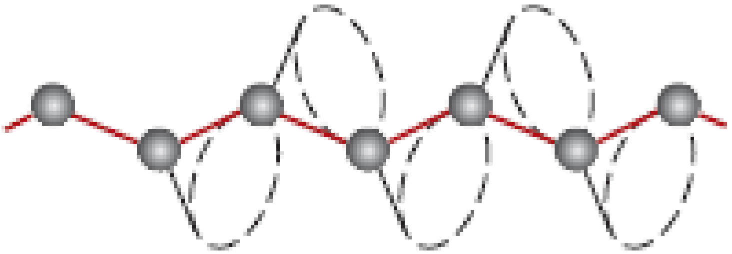
Weight Average

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
			$\overline{M}_w = \overline{23{,}200}$

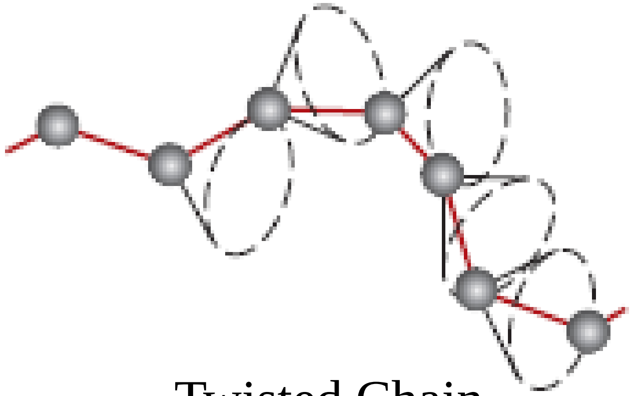
Polymer Shapes, Structures, Configurations



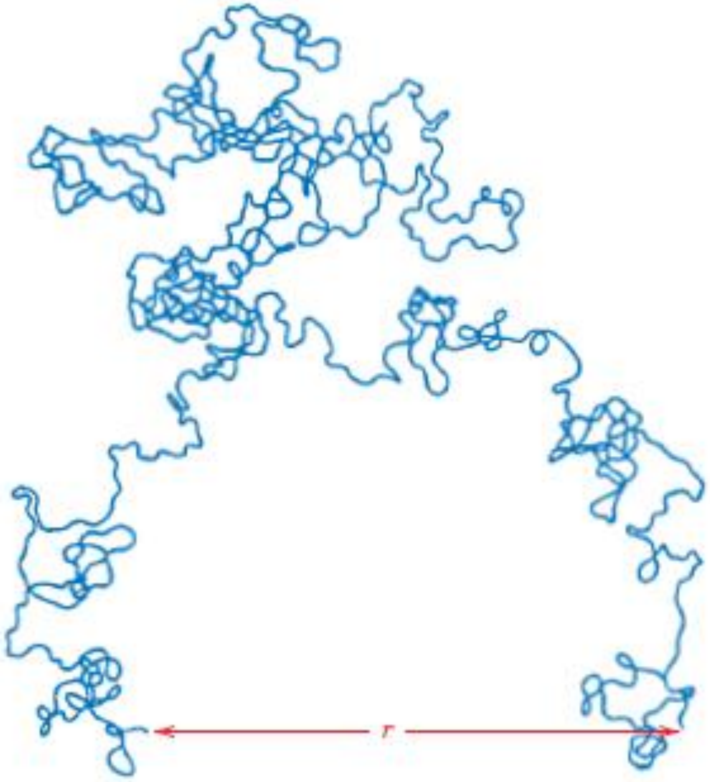
Infinite possibilities of keeping the third atom without violating the angle



Straight chain without any twists or kinks

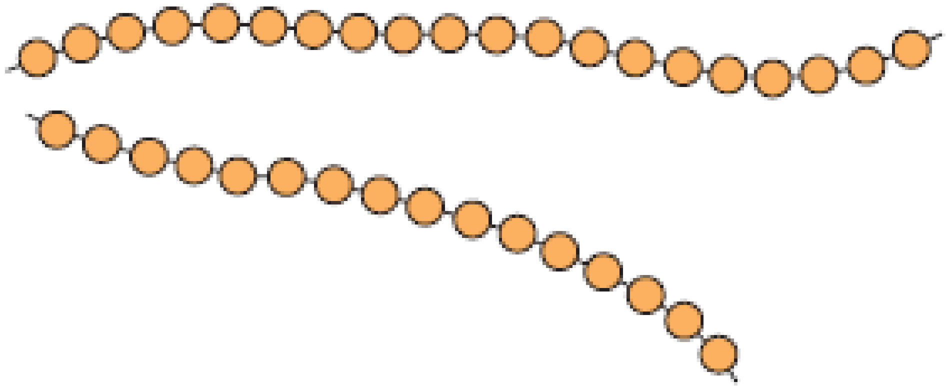


Twisted Chain

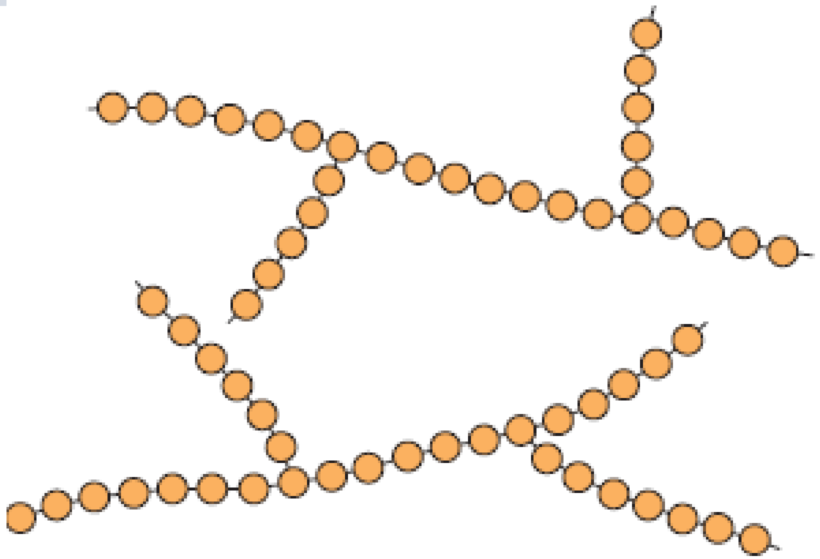


Schematic of the configuration of a long polymer chain

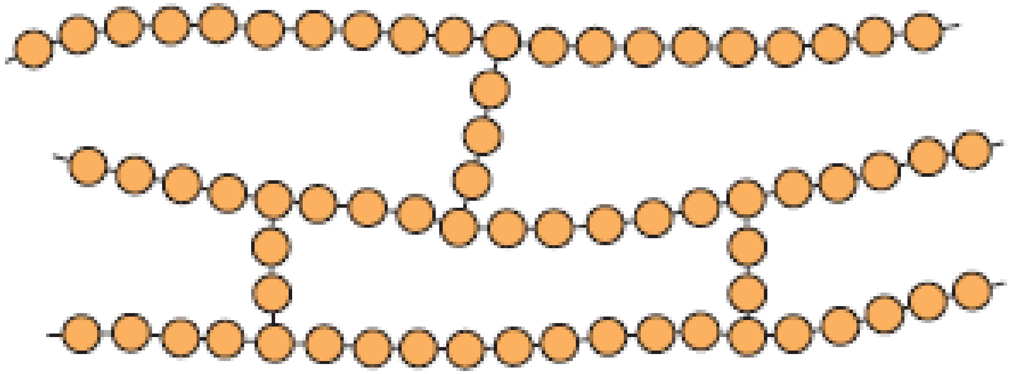
Polymer Shapes, Structures, Configurations



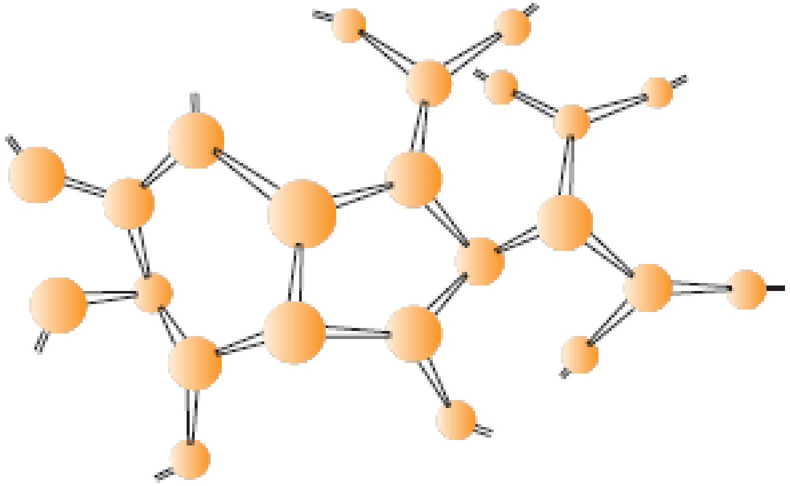
Linear Polymers, Ex. Polyethylene, PVC, nylon



Branched Polymers, Ex. LDPE

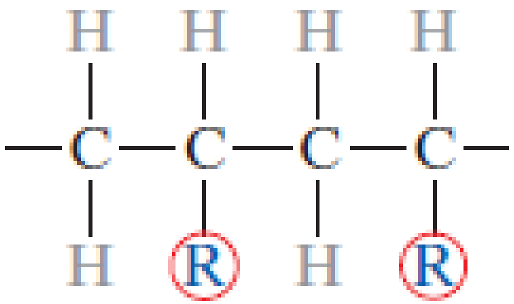


Cross–linked Polymers Ex. rubber

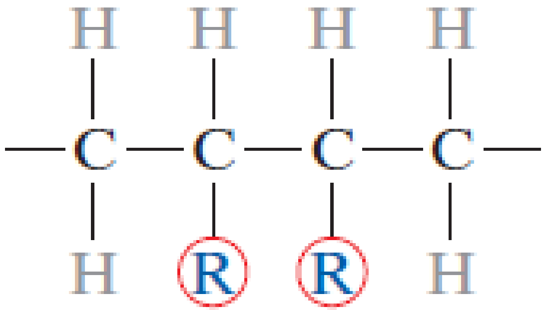


Network Polymers Ex. Epoxies, polyurethane, phenol-formaldehyde

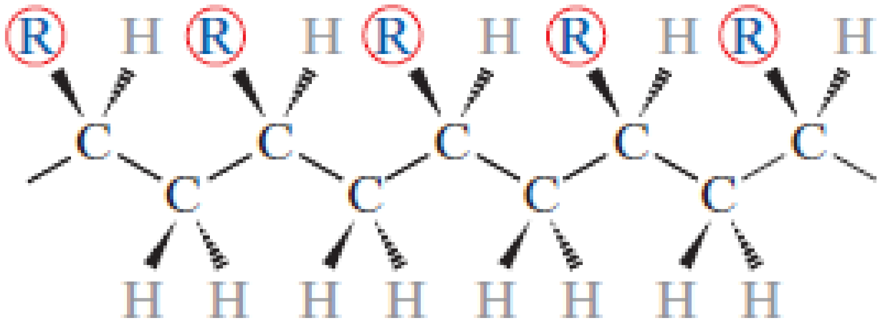
Polymer Shapes, Structures, Configurations



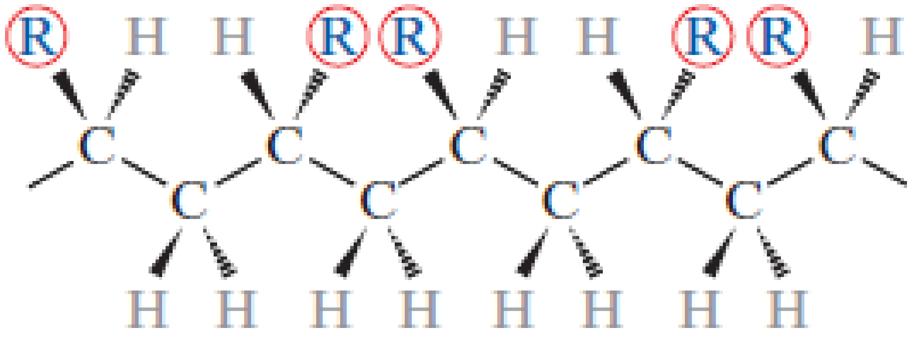
Head to Tail Configuration – more predominant



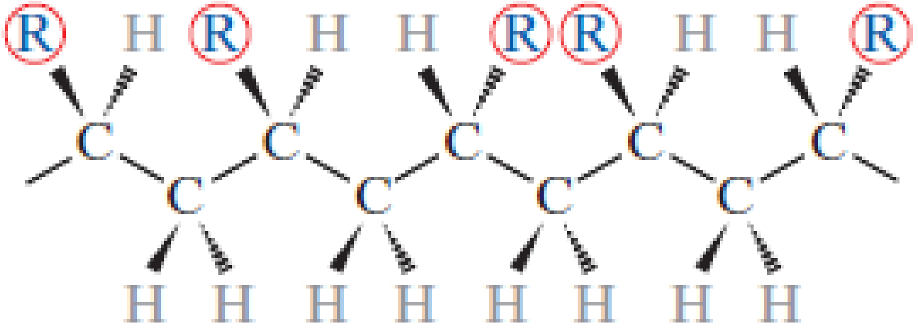
Head to Head Configuration



Isotactic configuration under Stereoisomerism



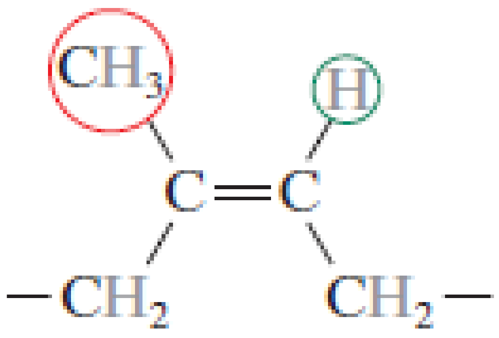
Syndiotactic configuration under Stereoisomerism



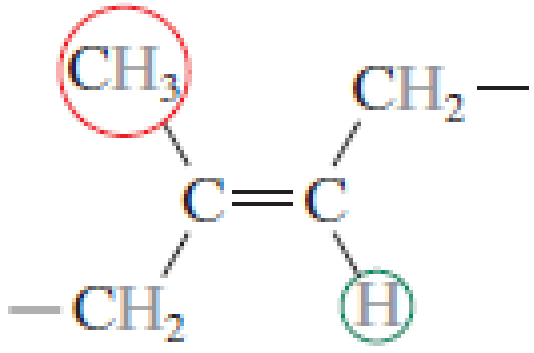
Atactic configuration under Stereoisomerism– Random Positioning

Polymer Shapes, Structures, Configurations

Geometrical Isomerism

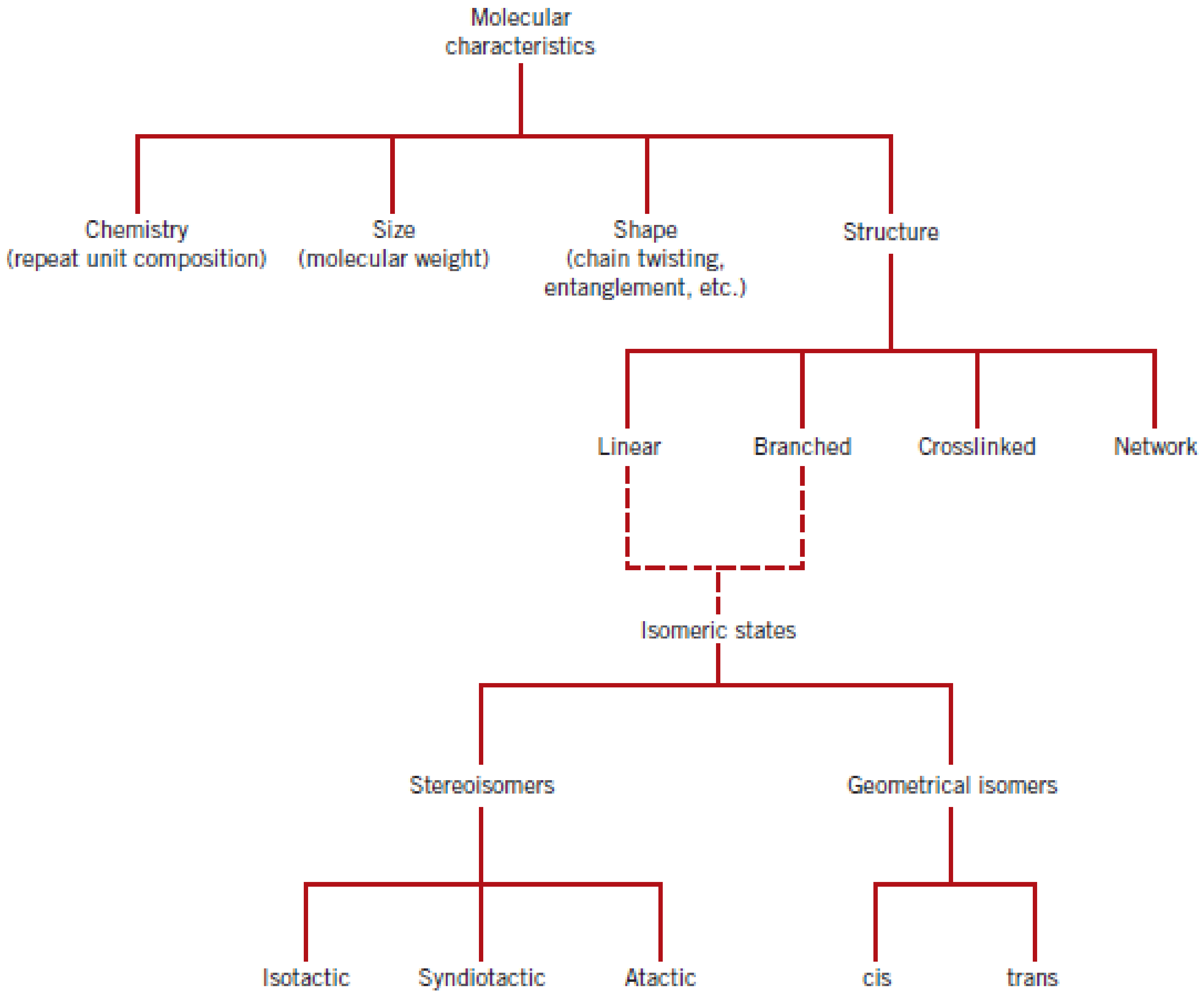


Cis Structure of Polyisoprene – natural rubber



Trans Structure of Polyisoprene

A Summary of Story So Far…



A Summary of Story So Far…

- Polymers are formed of repeat units, based on which they are classified as homopolymers and copolymers.
- Molecular weight of polymers affect their boiling point.
- Degree of polymerization represents average no of repeat units in polymer chains.
- Molecular shape relates to degree of chain twisting, coiling and bending.
- Molecular structure depends on how structural units are joined together.
- Molecular configuration refers to different isomeric configurations.
- These differences provide distinct properties to the same polymers.

Thermoplastic and Thermosetting Polymers

- **Thermoplastic** polymers are the ones that **soften upon heating** and **harden upon cooling** and **these changes are reversible**.

- Polyethylene, Polystyrene, Polyethylene terephthalate, Polyvinyl Chloride are some of the examples of thermoplastic polymers.

- **Thermosetting** polymers are the network polymers involving covalent cross–linking between adjacent chains. They harden upon formation and cannot be softened upon heating.

- Examples: Vulcanized rubbers, epoxies and phenolics and some polyester resins.

Polymer Crystallinity

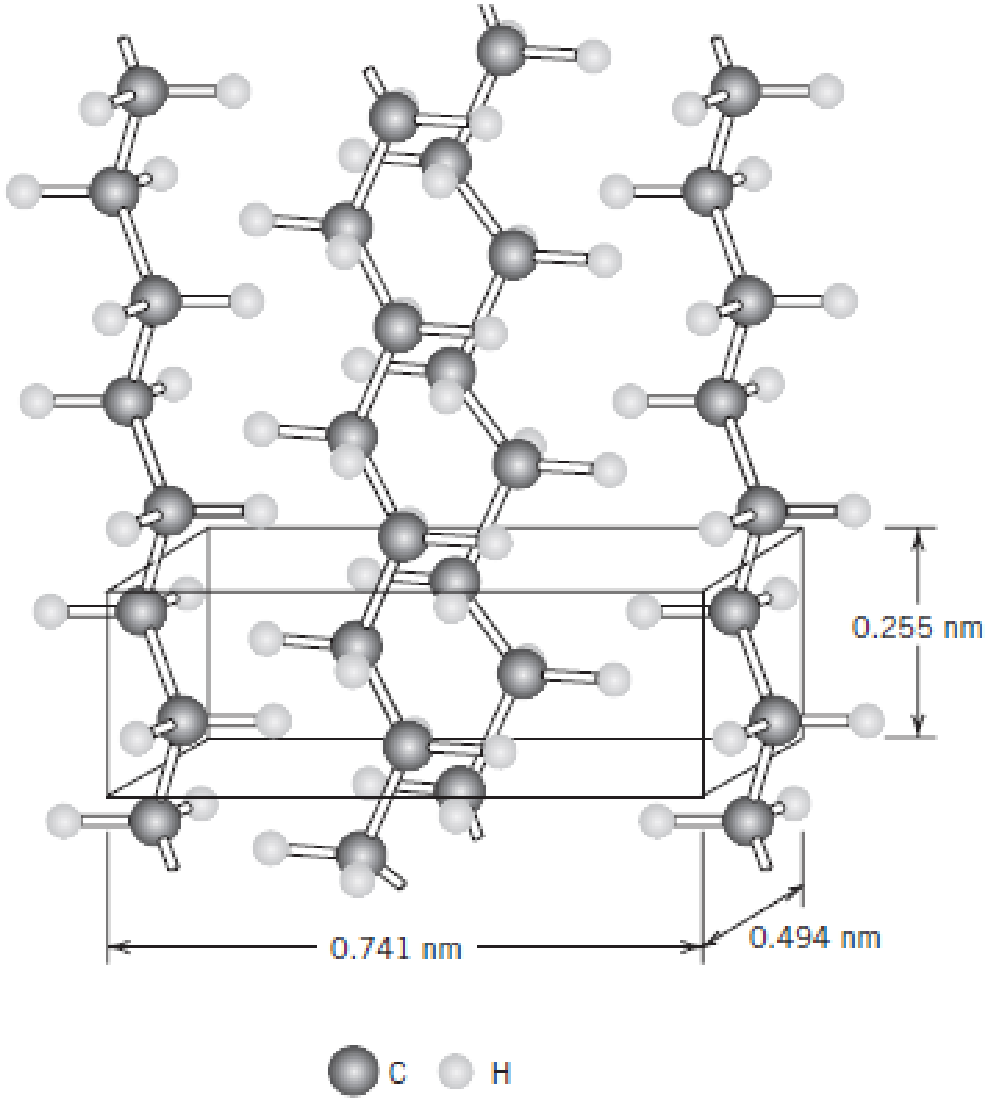
- Molecular substances of small molecules tend to form crystalline structures.

- The density of crystalline polymers are more than the amorphous ones of same molecular weight.

- Linear polymers tend to form crystalline structures upon controlled, slow cooling.

- Within stereoisomers, atactic polymers (being random) cannot attain crystallinity. Syndiotactic and isotactic can form crystalline structures.

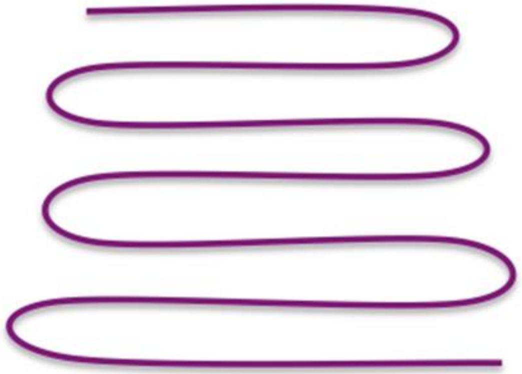
- Block copolymers have a tendency to form crystalline structures.



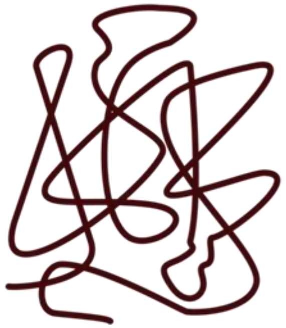
Polymer Crystallinity

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

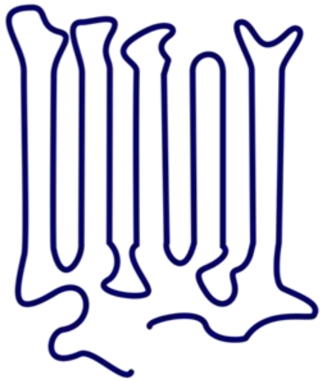
where ρ_s is the density of a specimen for which the percent crystallinity is to be determined, ρ_a is the density of the totally amorphous polymer, and ρ_c is the density of the perfectly crystalline polymer. The values of ρ_a and ρ_c must be measured by other experimental means.



Crystalline



Amorphous

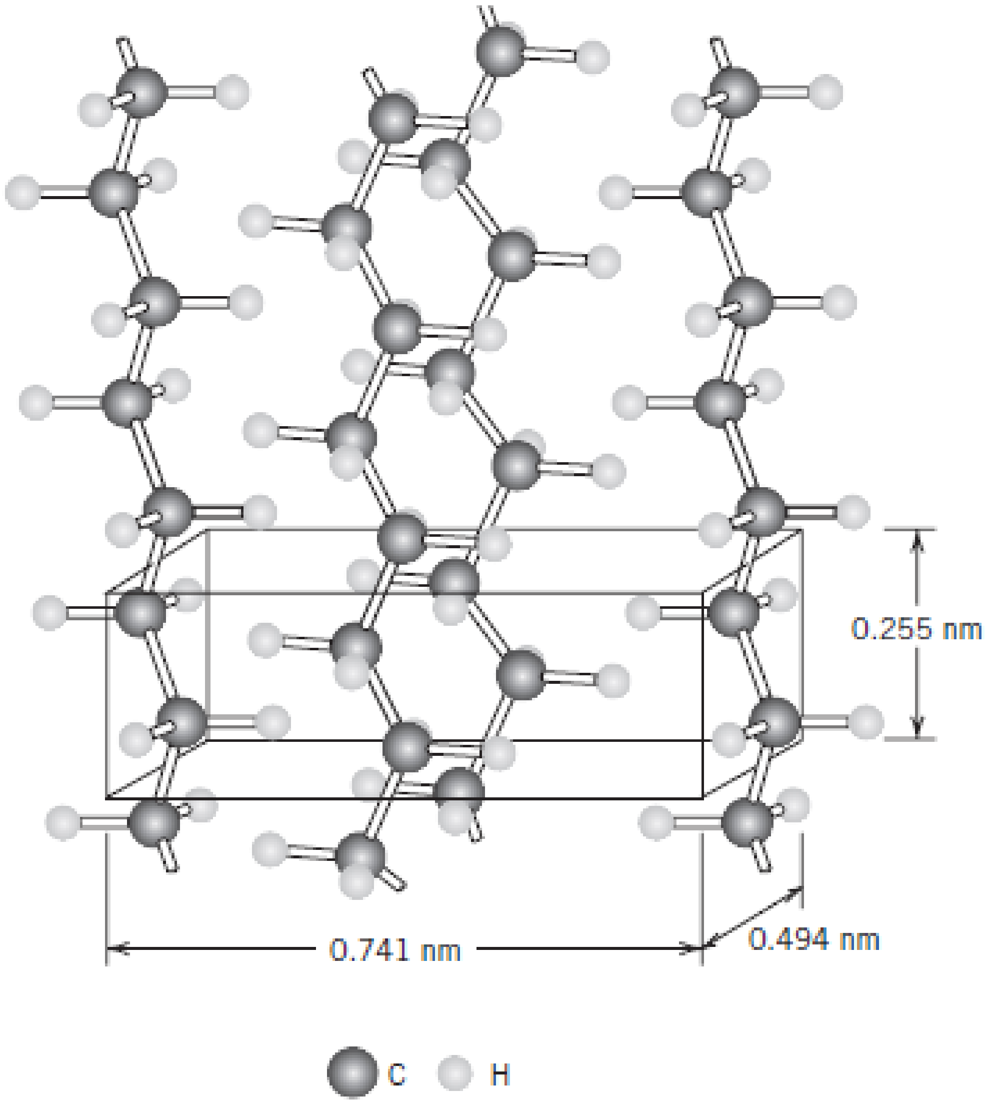


Semicrystalline

Computations of the Density and Percent Crystallinity of Polyethylene

(a) Compute the density of totally crystalline polyethylene. The orthorhombic unit cell for polyethylene is shown in below Figure; the equivalent of two ethylene repeat units is contained within each unit cell.

(b) Using the answer to part (a), calculate the percent crystallinity of a branched polyethylene that has a density of 0.925 g/cm3. The density for the totally amorphous material is 0.870 g/cm3.



$$\rho = \frac{nA}{V_C N_A}$$

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

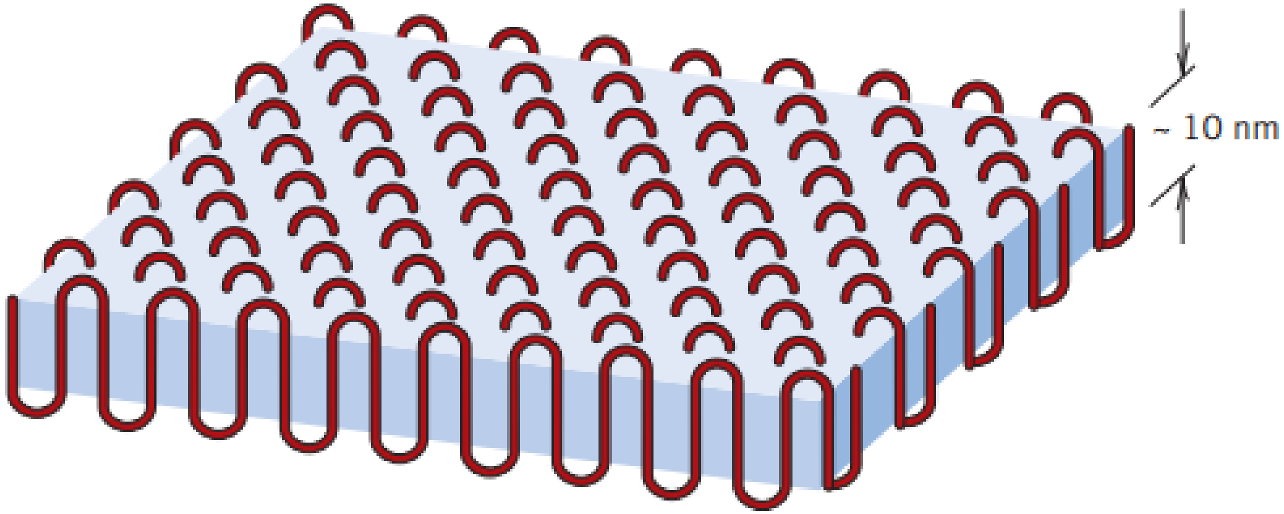
$$A = 2(A_{\mathrm{C}}) + 4(A_{\mathrm{H}})$$
$$= (2)(12.01\ \mathrm{g/mol}) + (4)(1.008\ \mathrm{g/mol}) = 28.05\ \mathrm{g/mol}$$

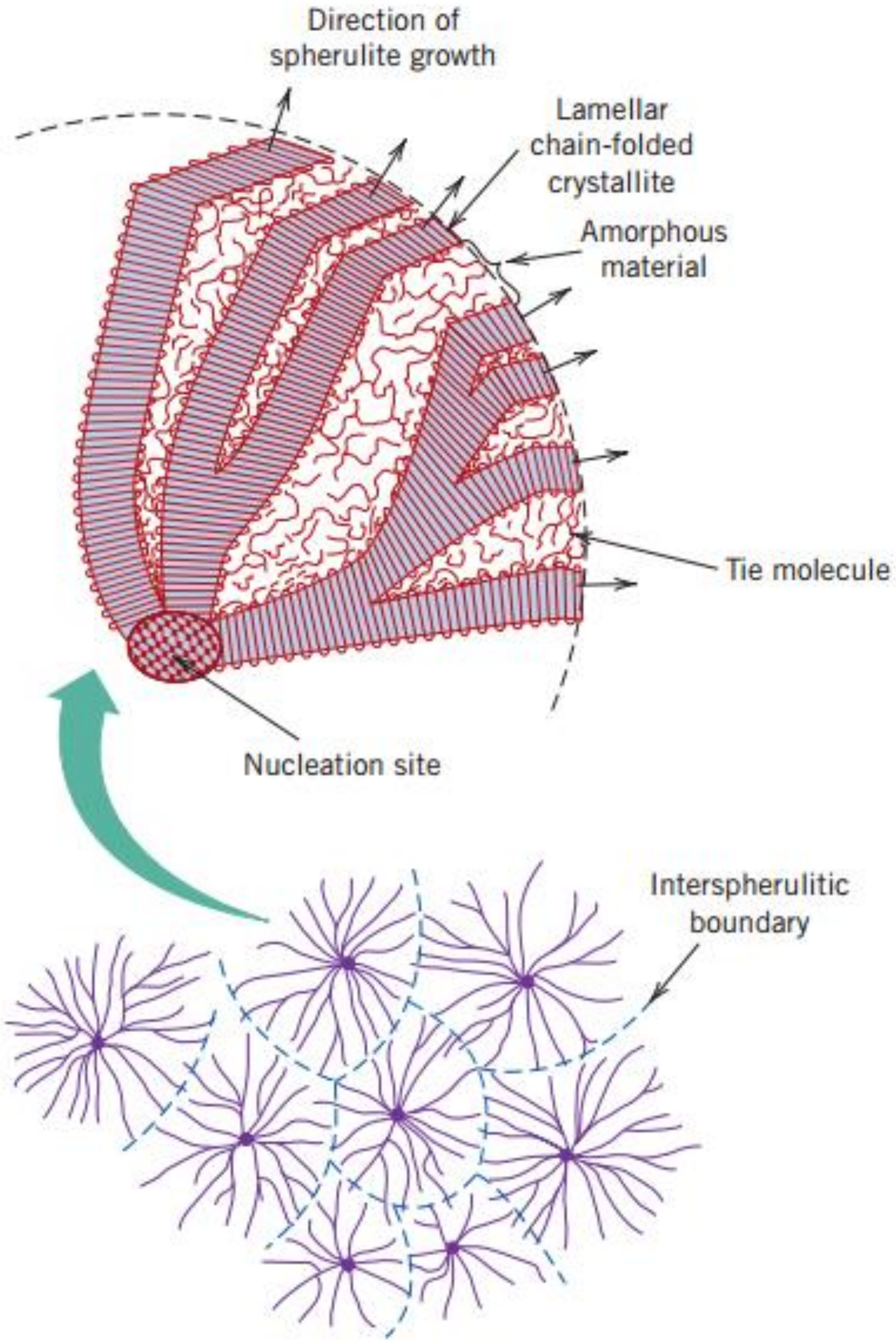
$$\begin{aligned} V_C &= (0.741\ \mathrm{nm})(0.494\ \mathrm{nm})(0.255\ \mathrm{nm}) \\ &= (7.41 \times 10^{-8}\ \mathrm{cm})(4.94 \times 10^{-8}\ \mathrm{cm})(2.55 \times 10^{-8}\ \mathrm{cm}) \\ &= 9.33 \times 10^{-23}\ \mathrm{cm^3/unit\ cell} \end{aligned}$$

$$\begin{aligned} \rho &= \frac{nA}{V_C N_{\mathrm{A}}} \\ &= \frac{(2\ \text{repeat units/unit cell})(28.05\ \mathrm{g/mol})}{(9.33 \times 10^{-23}\ \mathrm{cm^3/unit\ cell})(6.022 \times 10^{23}\ \text{repeat units/mol})} \\ &= 0.998\ \mathrm{g/cm^3} \end{aligned}$$

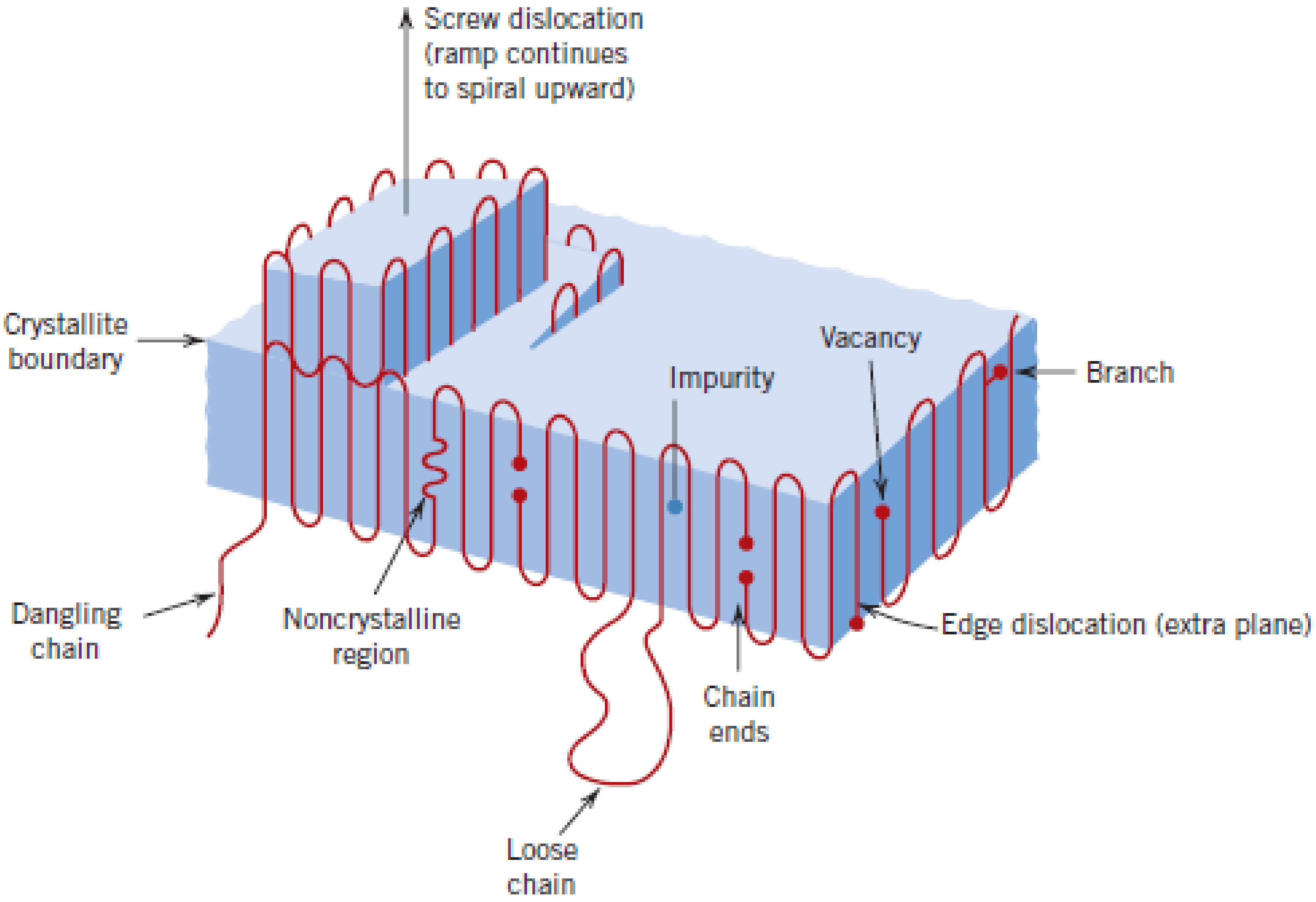
$$\begin{aligned} \%\ \text{crystallinity} &= \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100 \\ &= \frac{0.998\ \mathrm{g/cm^3}\ (0.925\ \mathrm{g/cm^3} - 0.870\ \mathrm{g/cm^3})}{0.925\ \mathrm{g/cm^3}\ (0.998\ \mathrm{g/cm^3} - 0.870\ \mathrm{g/cm^3})} \times 100 \\ &= 46.4\% \end{aligned}$$

Crystal structure in polymers



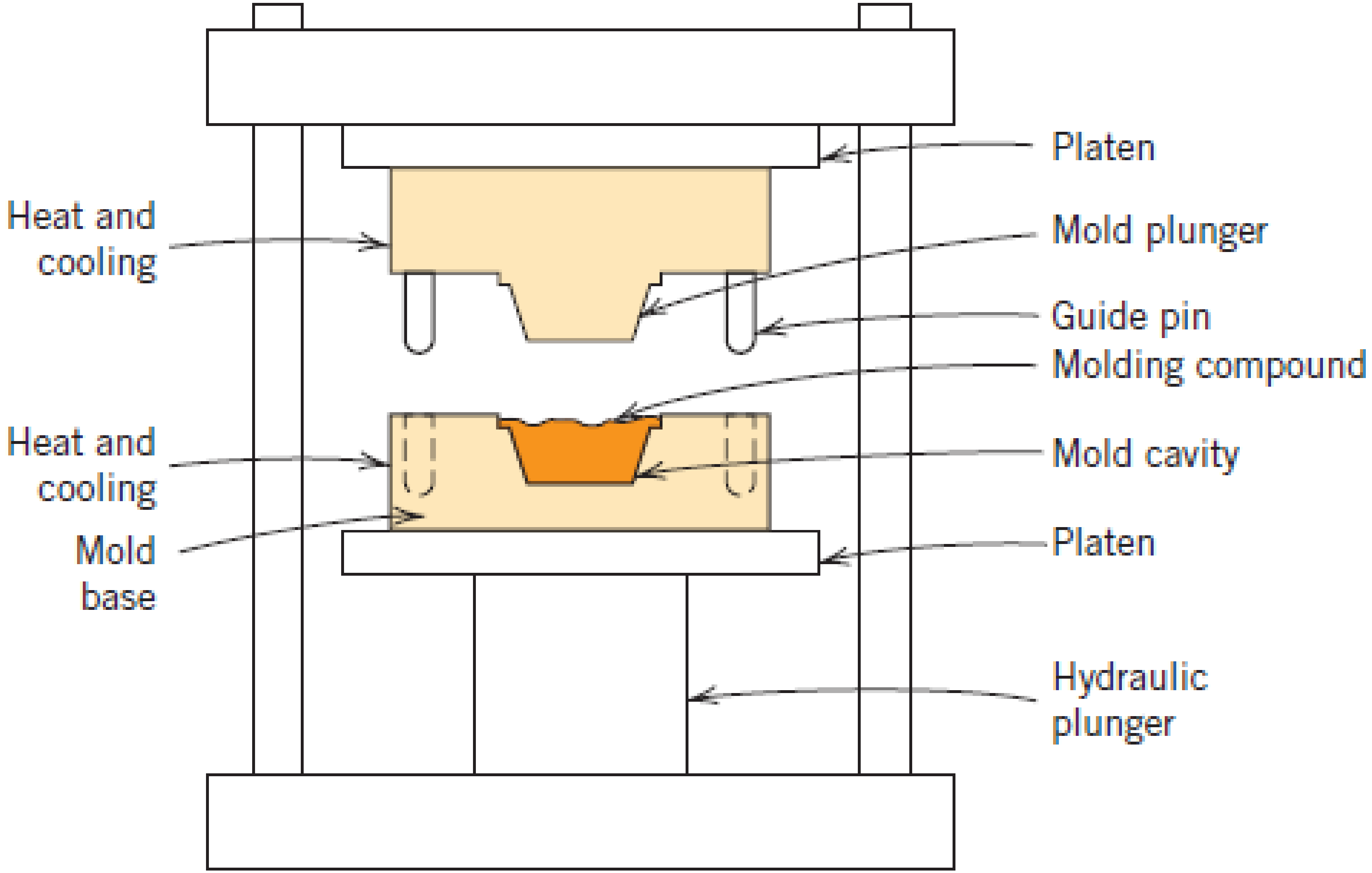


Defects in polymers



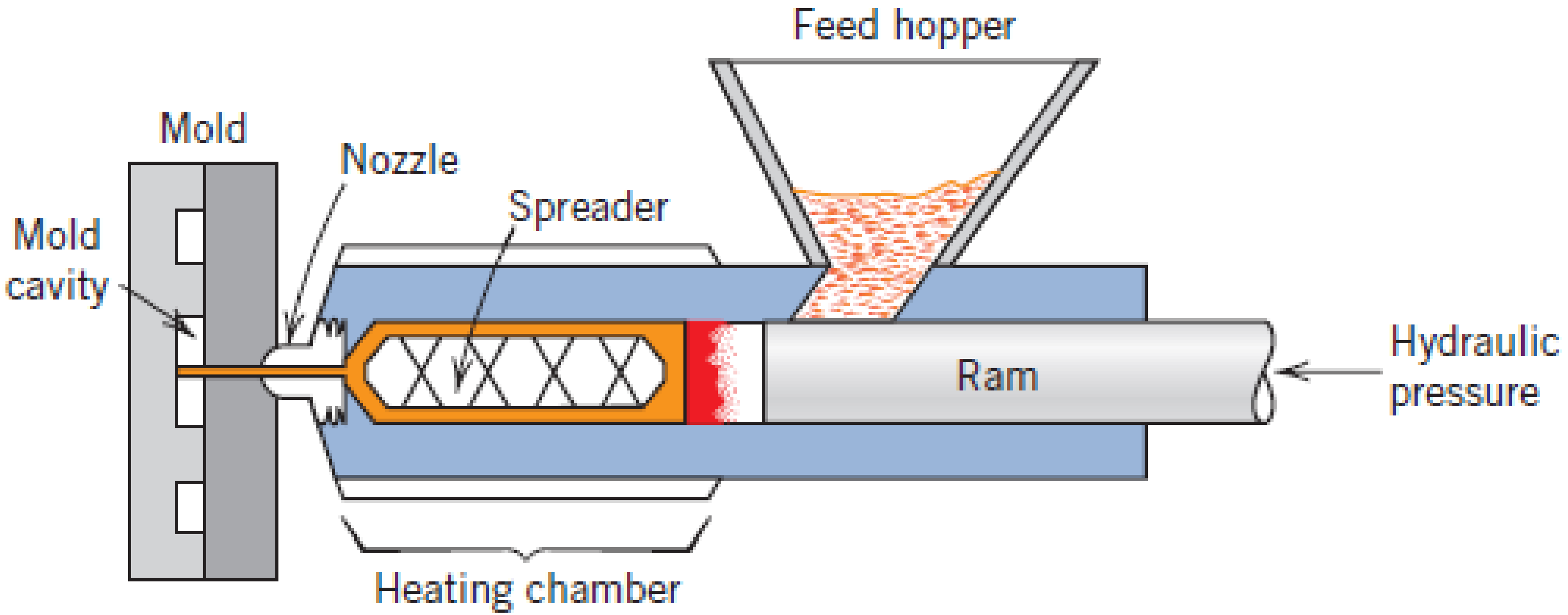
Forming Techniques for Plastics

Compression molding

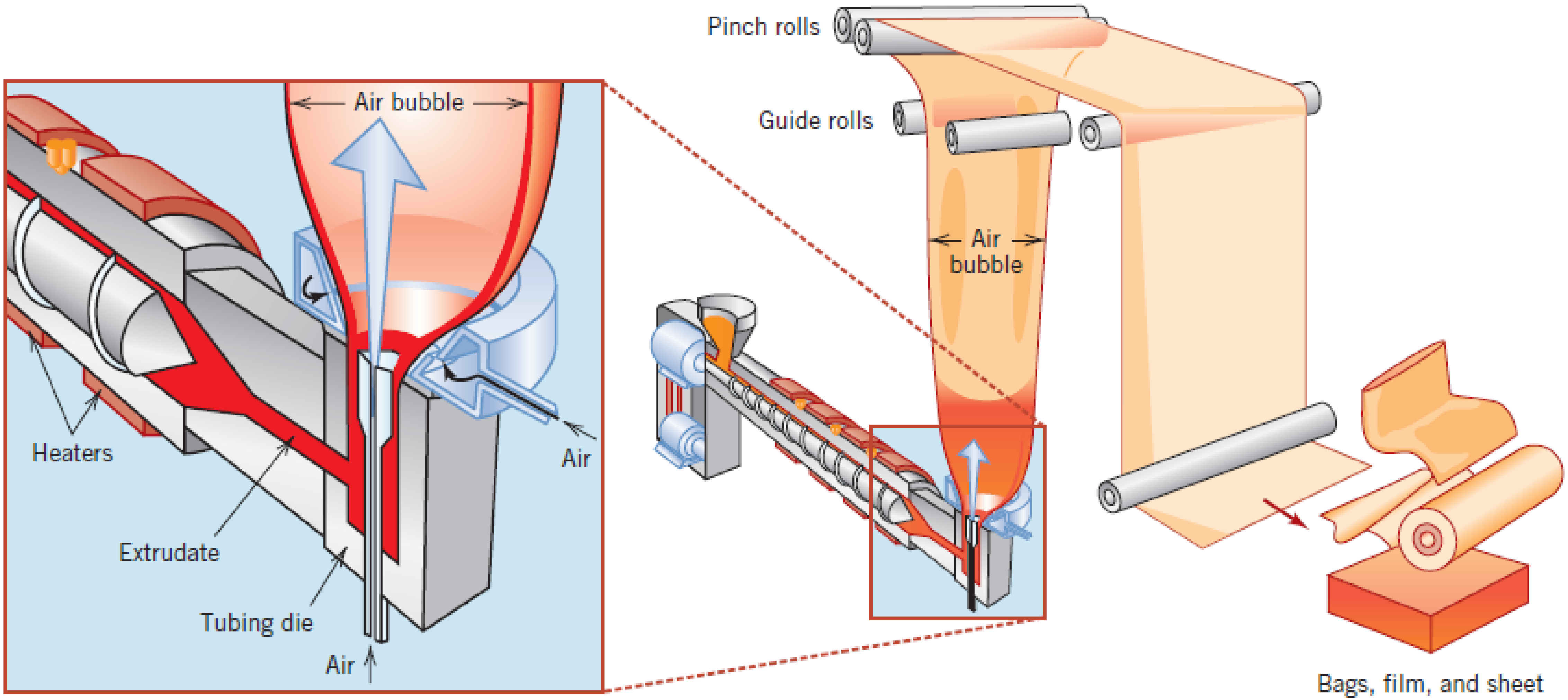


Forming Techniques for Plastics

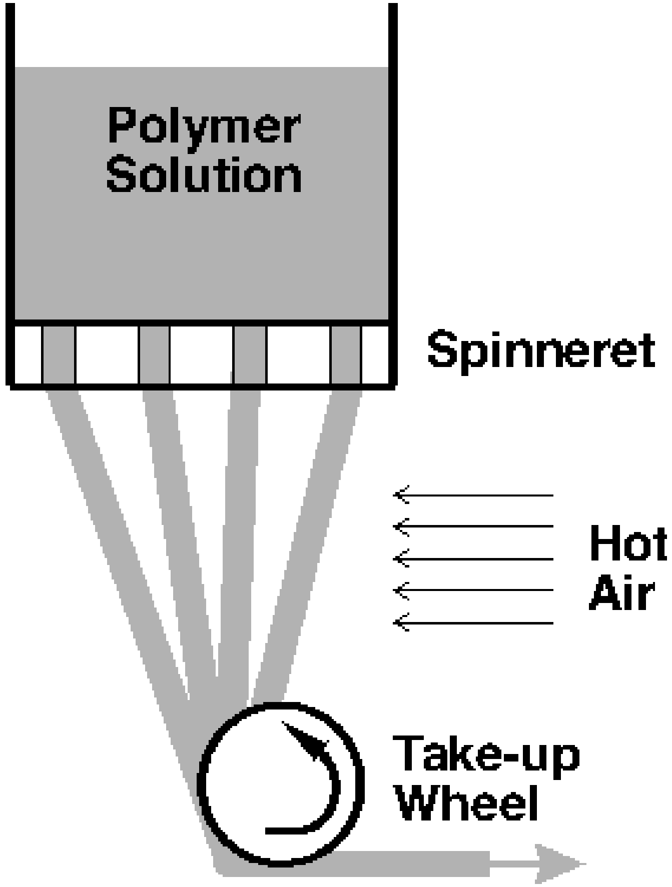
Injection molding



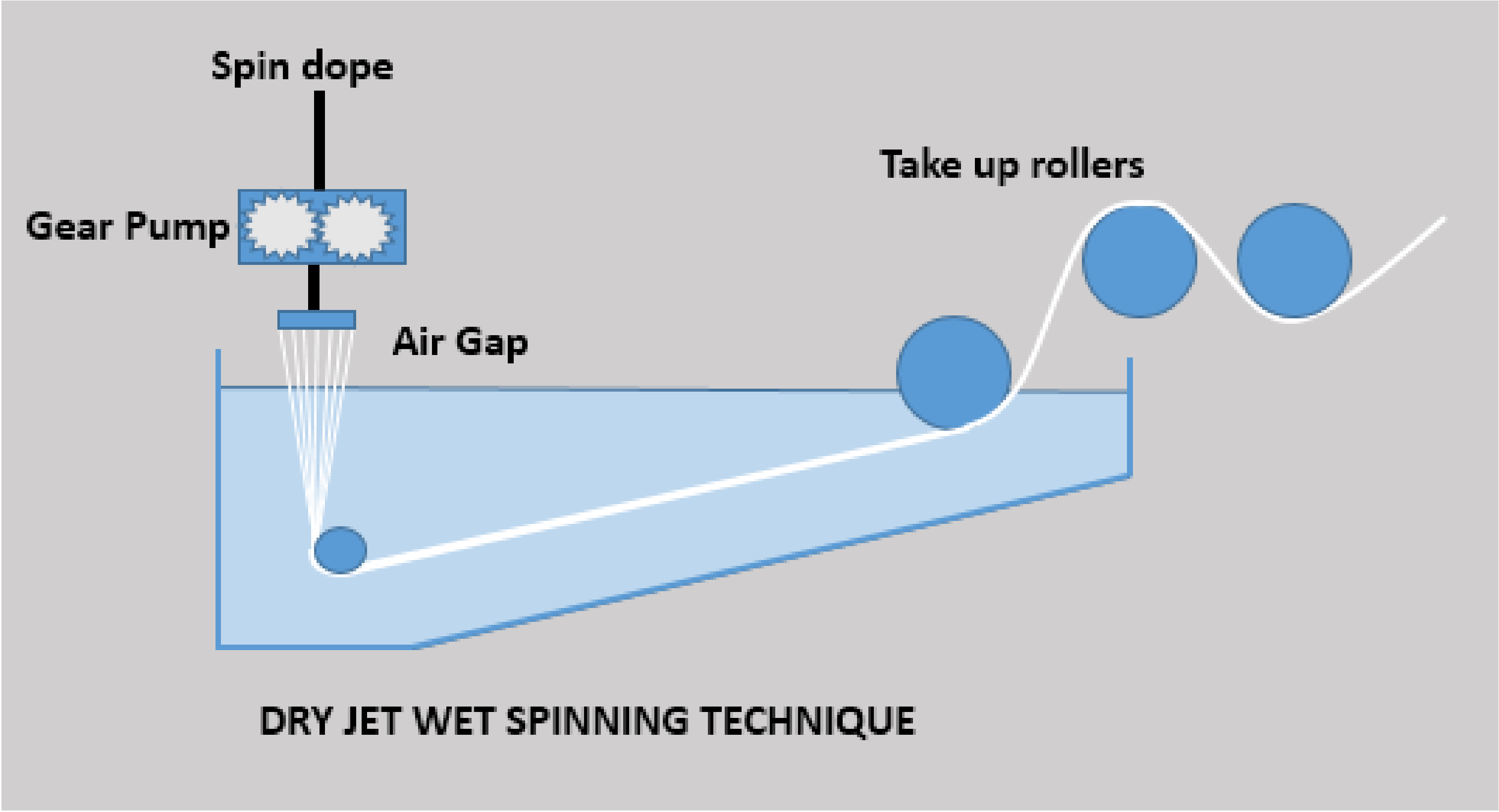
Polymer Films



Fibers by Spinning



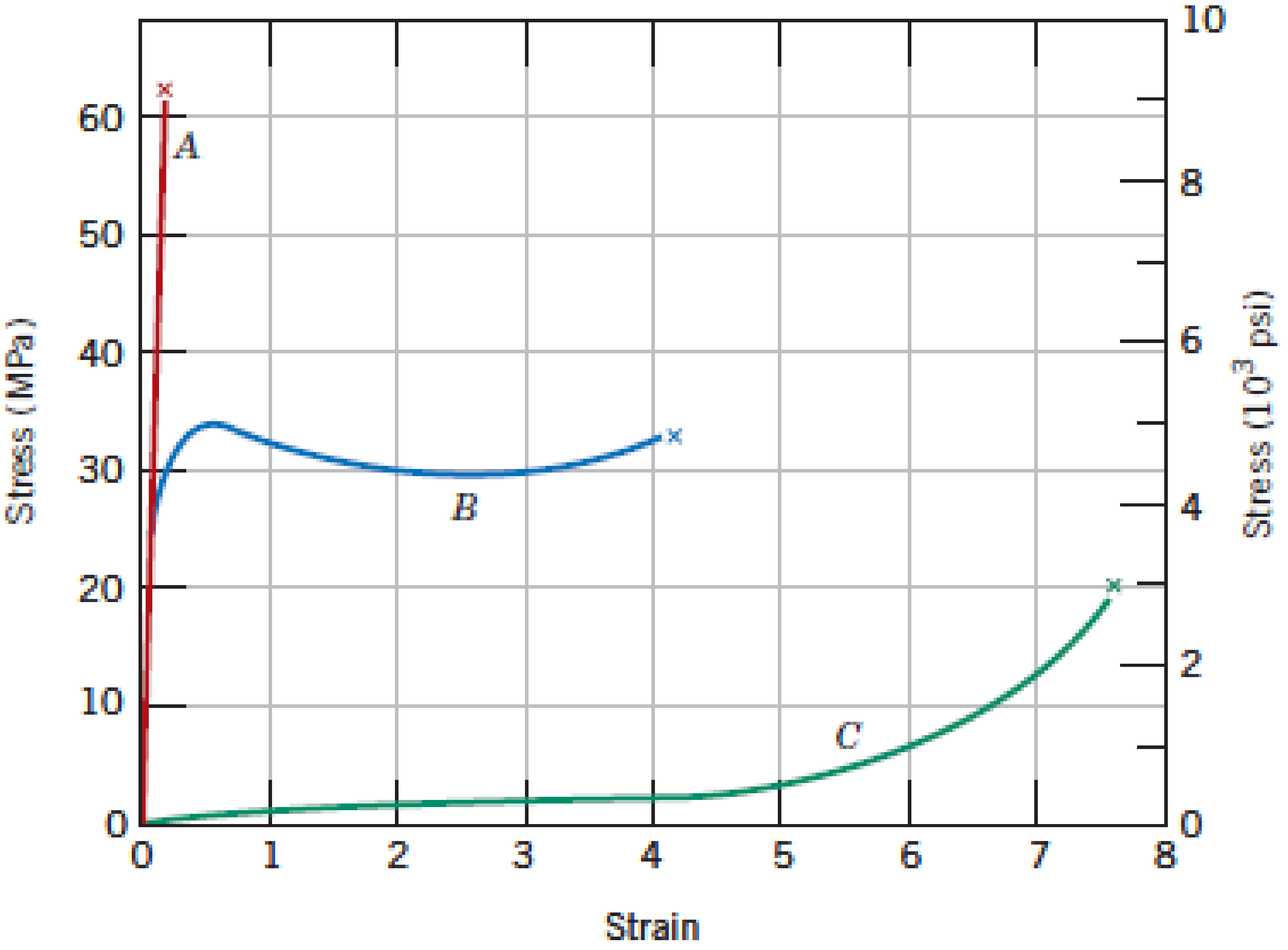
Dry Spinning



Wet Spinning

Mechanical Behaviour of Polymers

- Curve A – Brittle
- Curve B – Elastic-Plastic
- Curve C – Highly Elastic (Elastomers)

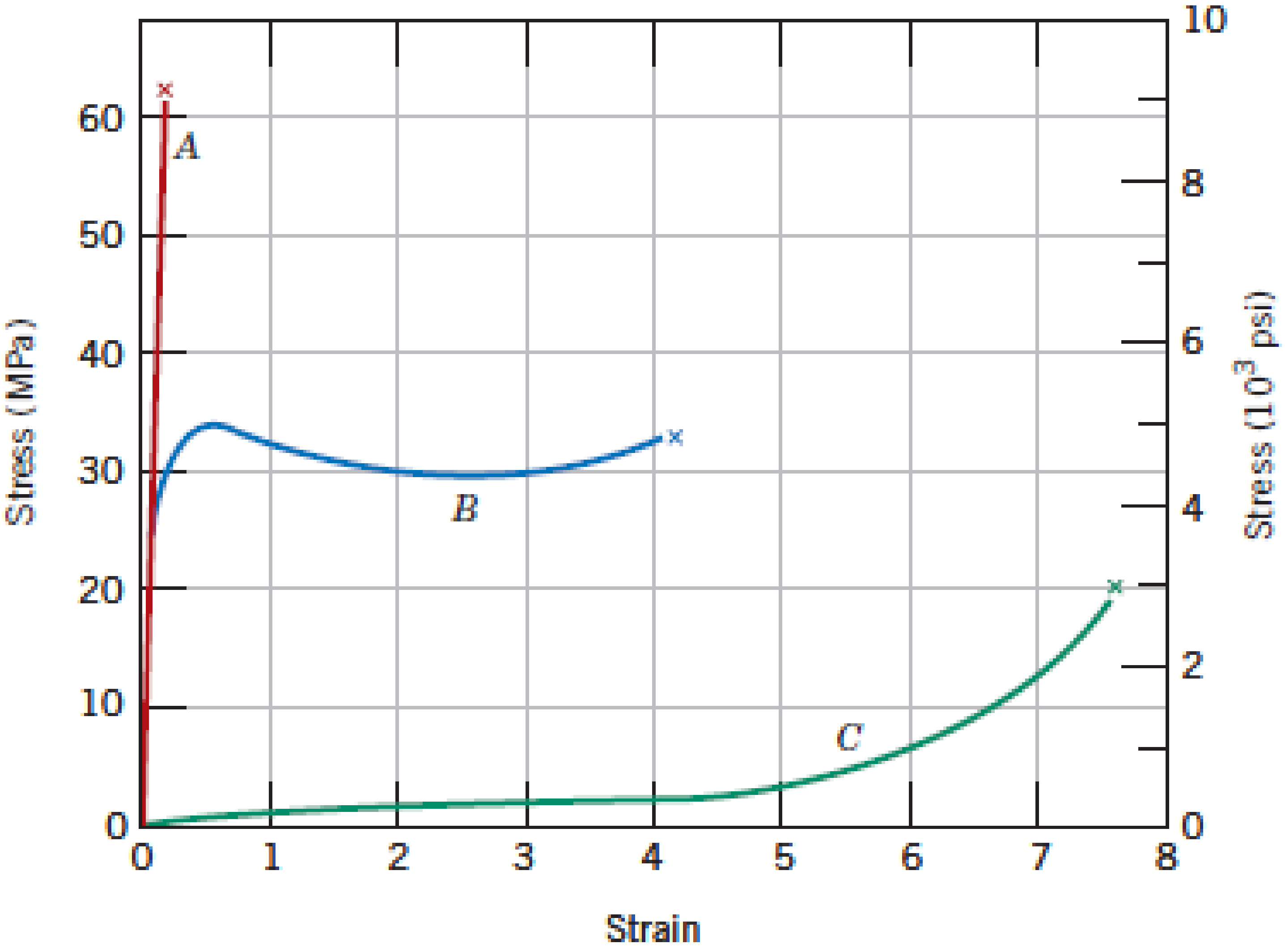


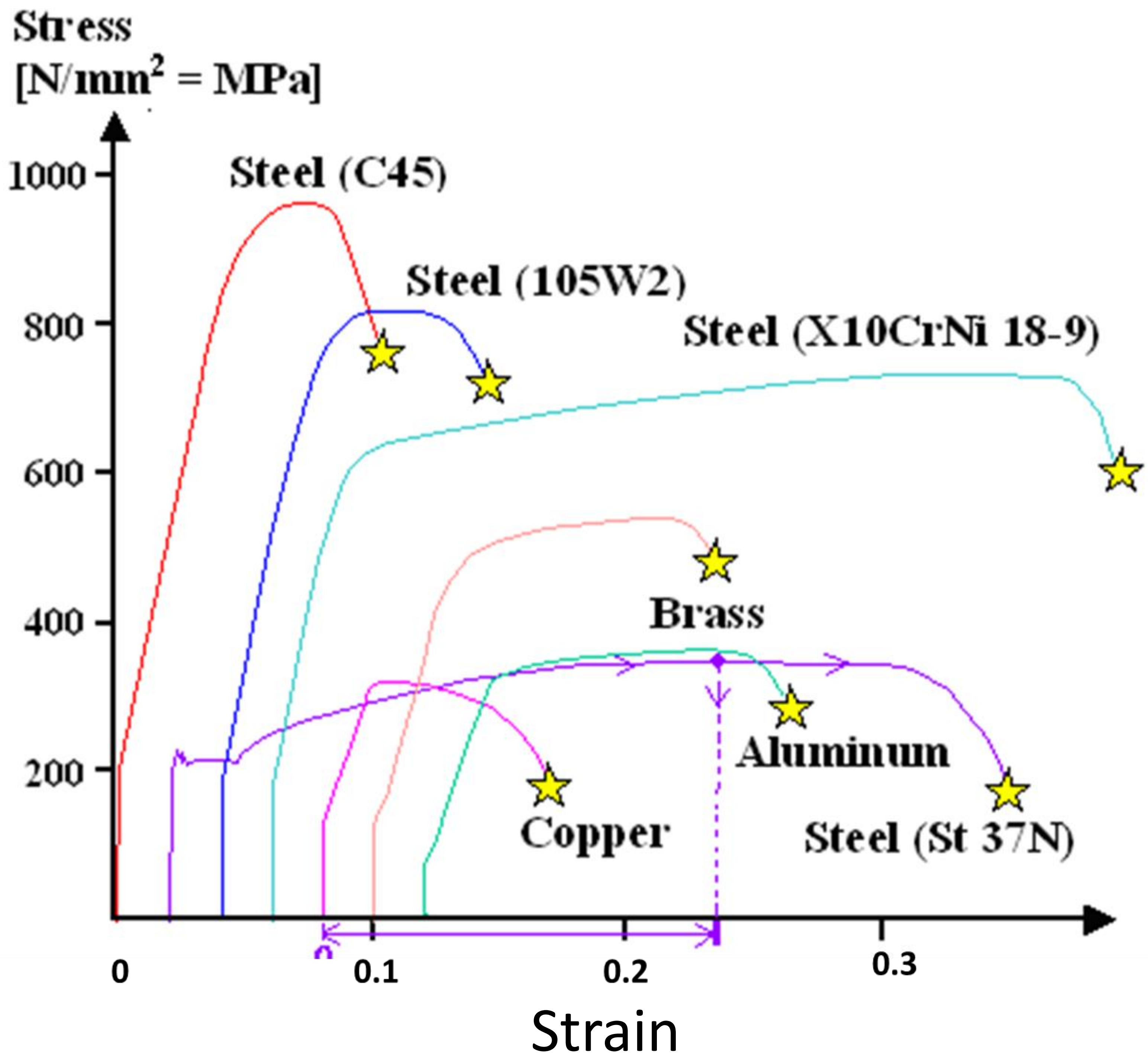
Mechanical Behaviour of Polymers

• Fracture strengths of polymers ~ 1 to10% of those for metals

• Deformation strains for polymers > 1000%

– for most metals, deformation strains < 10%




Stress
[N/mm² = MPa]
1000
800
600
400
200
Steel (C45)
Steel (105W2)
Steel (X10CrNi 18-9)
Brass
Aluminum
Copper
Steel (St 37N)
0
0.1
0.2
0.3
Strain

Mechanical Behaviour of Polymers

Material	*Specific Gravity*	*Tensile Modulus [GPa (ksi)]*	*Tensile Strength [MPa (ksi)]*	*Yield Strength [MPa (ksi)]*	*Elongation at Break (%)*
Polyethylene (low density)	0.917–0.932	0.17–0.28 (25–41)	8.3–31.4 (1.2–4.55)	9.0–14.5 (1.3–2.1)	100–650
Polyethylene (high density)	0.952–0.965	1.06–1.09 (155–158)	22.1–31.0 (3.2–4.5)	26.2–33.1 (3.8–4.8)	10–1200
Poly(vinyl chloride)	1.30–1.58	2.4–4.1 (350–600)	40.7–51.7 (5.9–7.5)	40.7–44.8 (5.9–6.5)	40–80
Polytetrafluoroethylene	2.14–2.20	0.40–0.55 (58–80)	20.7–34.5 (3.0–5.0)	—	200–400
Polypropylene	0.90–0.91	1.14–1.55 (165–225)	31–41.4 (4.5–6.0)	31.0–37.2 (4.5–5.4)	100–600
Polystyrene	1.04–1.05	2.28–3.28 (330–475)	35.9–51.7 (5.2–7.5)	—	1.2–2.5
Poly(methyl methacrylate)	1.17–1.20	2.24–3.24 (325–470)	48.3–72.4 (7.0–10.5)	53.8–73.1 (7.8–10.6)	2.0–5.5
Phenol-formaldehyde	1.24–1.32	2.76–4.83 (400–700)	34.5–62.1 (5.0–9.0)	—	1.5–2.0
Nylon 6,6	1.13–1.15	1.58–3.80 (230–550)	75.9–94.5 (11.0–13.7)	44.8–82.8 (6.5–12)	15–300
Polyester (PET)	1.29–1.40	2.8–4.1 (400–600)	48.3–72.4 (7.0–10.5)	59.3 (8.6)	30–300
Polycarbonate	1.20	2.38 (345)	62.8–72.4 (9.1–10.5)	62.1 (9.0)	110–150

Mechanical Properties of Metals

Metal Alloy	*Yield Strength, MPa (ksi)*	*Tensile Strength, MPa (ksi)*	*Ductility, %EL [in 50 mm (2 in.)]*
Aluminum	35 (5)	90 (13)	40
Copper	69 (10)	200 (29)	45
Brass (70Cu–30Zn)	75 (11)	300 (44)	68
Iron	130 (19)	262 (38)	45
Nickel	138 (20)	480 (70)	40
Steel (1020)	180 (26)	380 (55)	25
Titanium	450 (65)	520 (75)	25
Molybdenum	565 (82)	655 (95)	35

	Modulus of Elasticity		*Shear Modulus*		
Metal Alloy	*GPa*	*10^6 psi*	*GPa*	*10^6 psi*	*Poisson's Ratio*
Aluminum	69	10	25	3.6	0.33
Brass	97	14	37	5.4	0.34
Copper	110	16	46	6.7	0.34
Magnesium	45	6.5	17	2.5	0.29
Nickel	207	30	76	11.0	0.31
Steel	207	30	83	12.0	0.30
Titanium	107	15.5	45	6.5	0.34
Tungsten	407	59	160	23.2	0.28

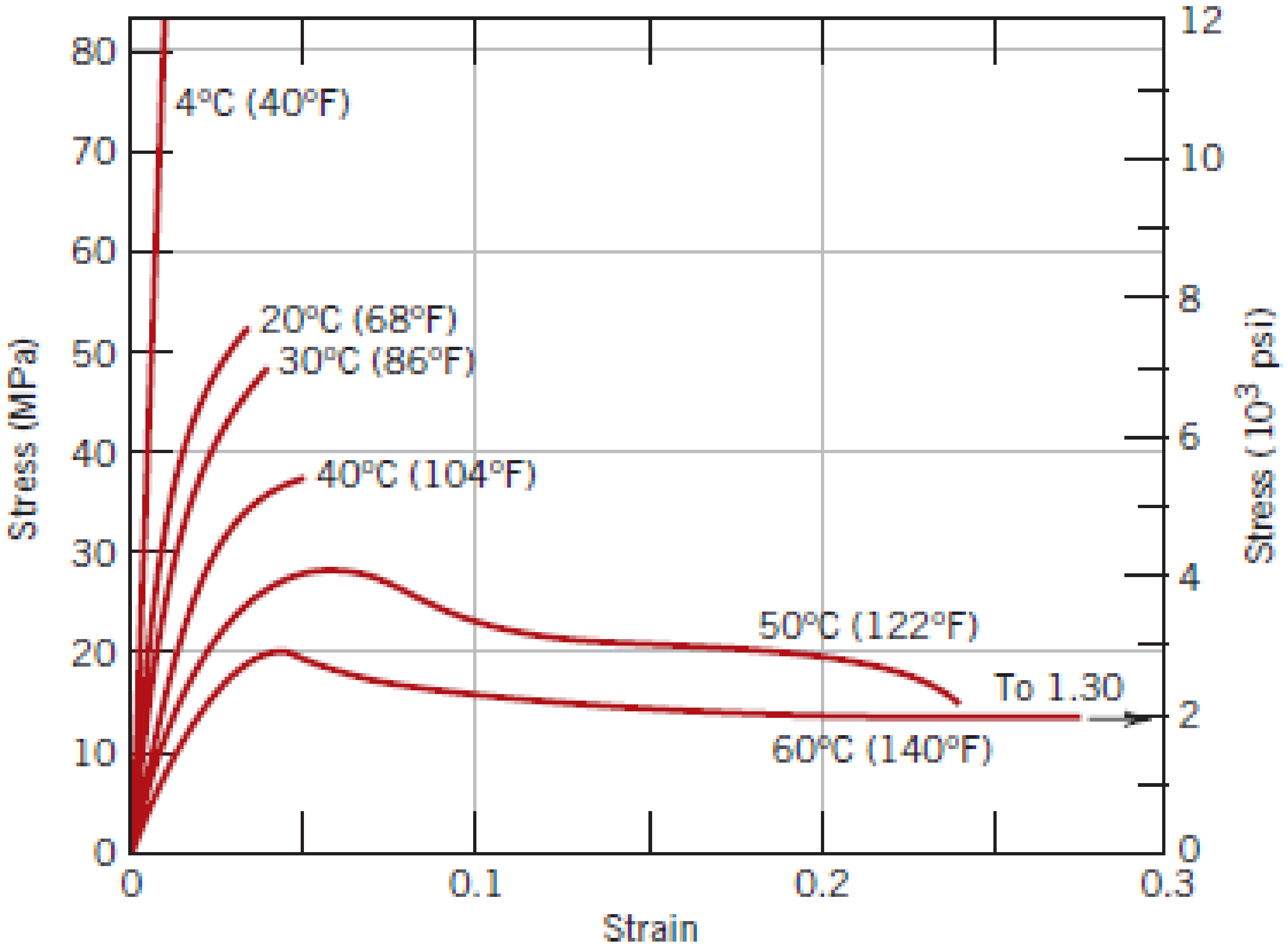
Mechanical Behaviour of Polymers – Influence of Temperature & Strain Rate

- In addition to yield strength and ductility, Elastic modulus also changes (decreases with increase in temperature).

- Stress – Strain curves shown in the adjacent figure are for PMMA.

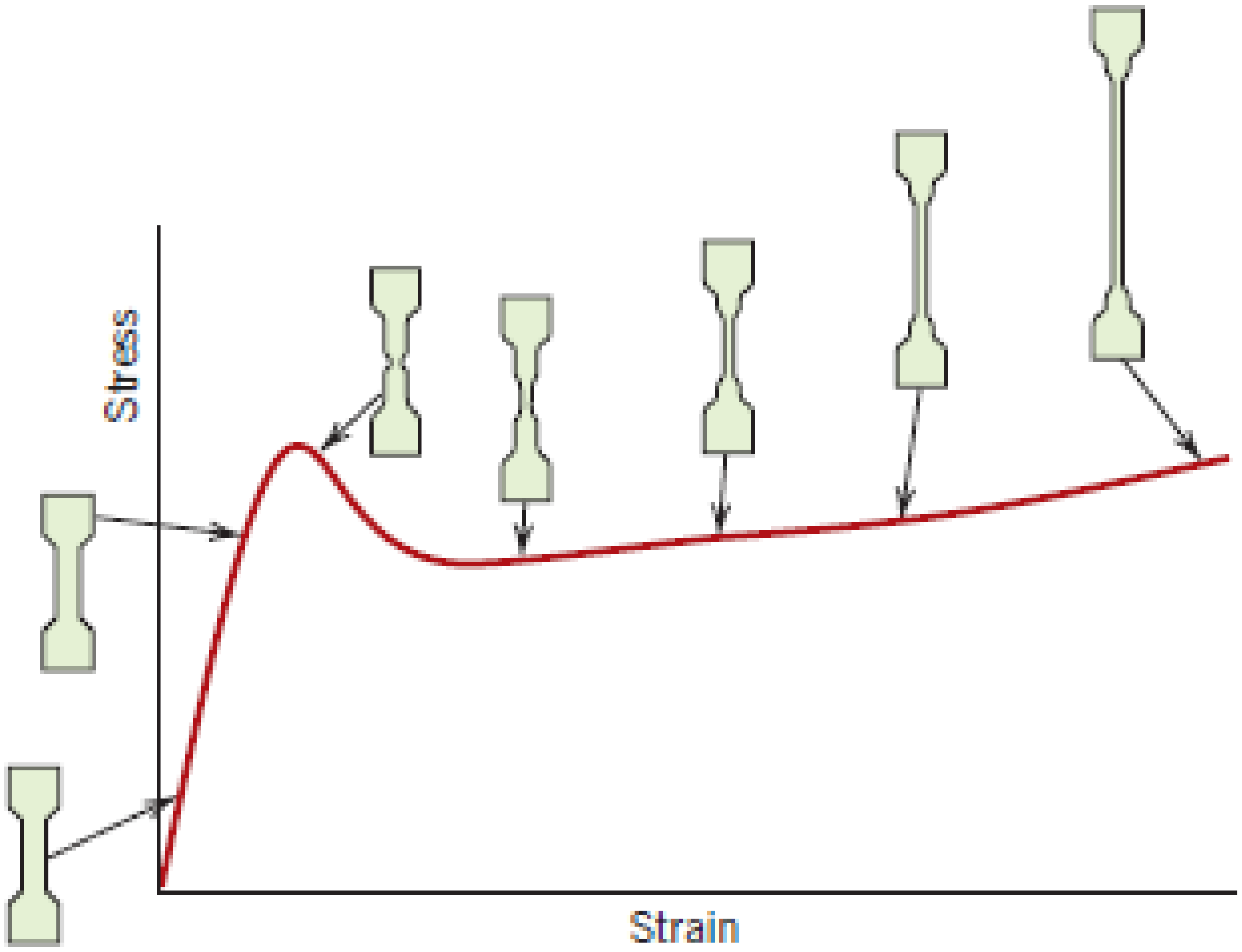
- T_g for PMMA is 105^0C.

- Decreasing the rate of strain applied has the same influence as increasing the temperature.

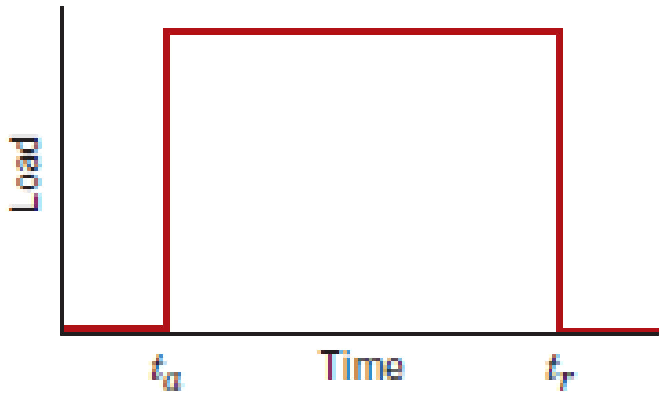


Macroscopic Deformation

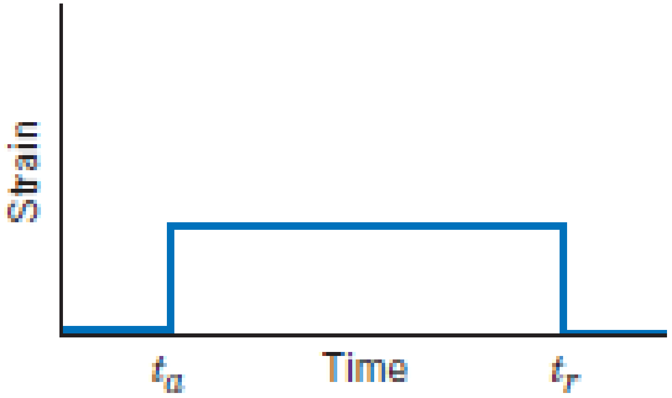
Semi–crystalline polymers undergo very large strains and have stress–strain curves as shown in the figure below.



Viscoelastic Deformation

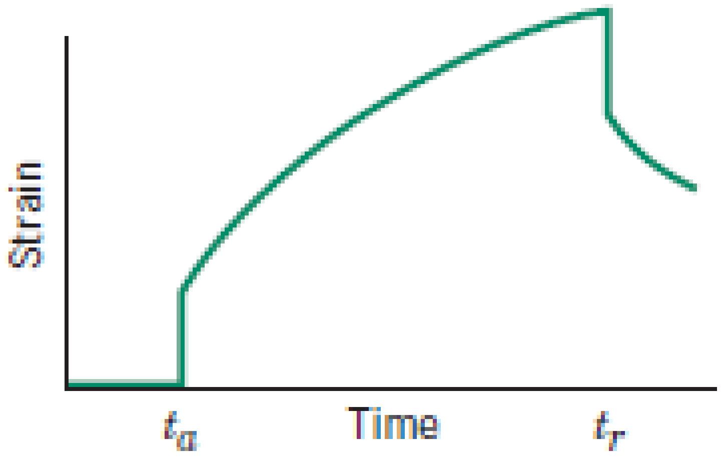


Applied loading history

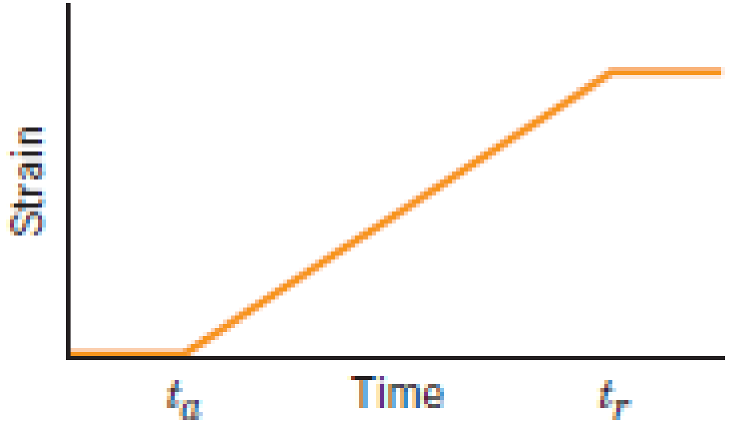


The response Strain history for an elastic solid

https://meet.google.com/gph-rdjg-pfm



The response Strain history for a viscoelastic solid



The response Strain history for a viscous medium

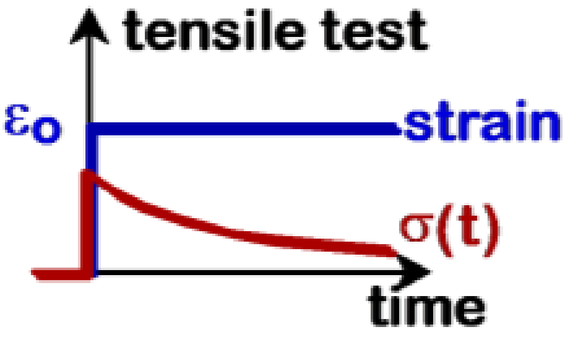
Viscoelasticity: Relaxation Modulus

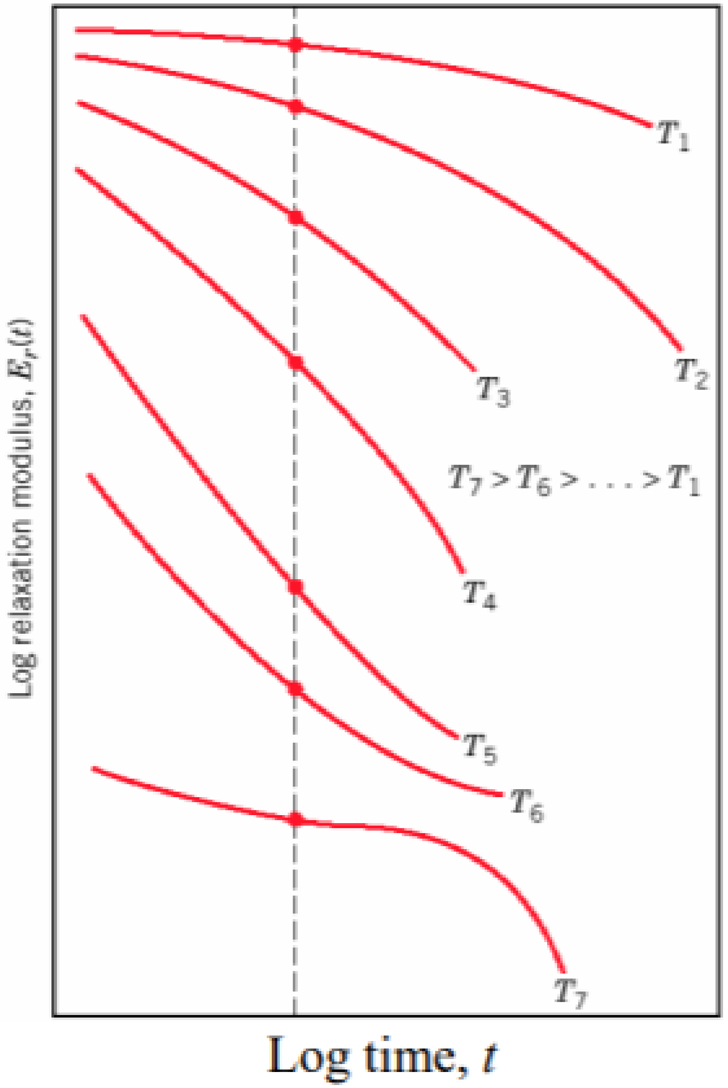
Viscoelasticity can be characterized by the **viscoelastic relaxation modulus**:

- Sample is strained rapidly to pre-determined strain.
- Stress required to maintain this strain ε_0 over time is measured at constant T.
- Stress decreases with time due to molecular relaxation processes.
- Relaxation modulus can be defined as:

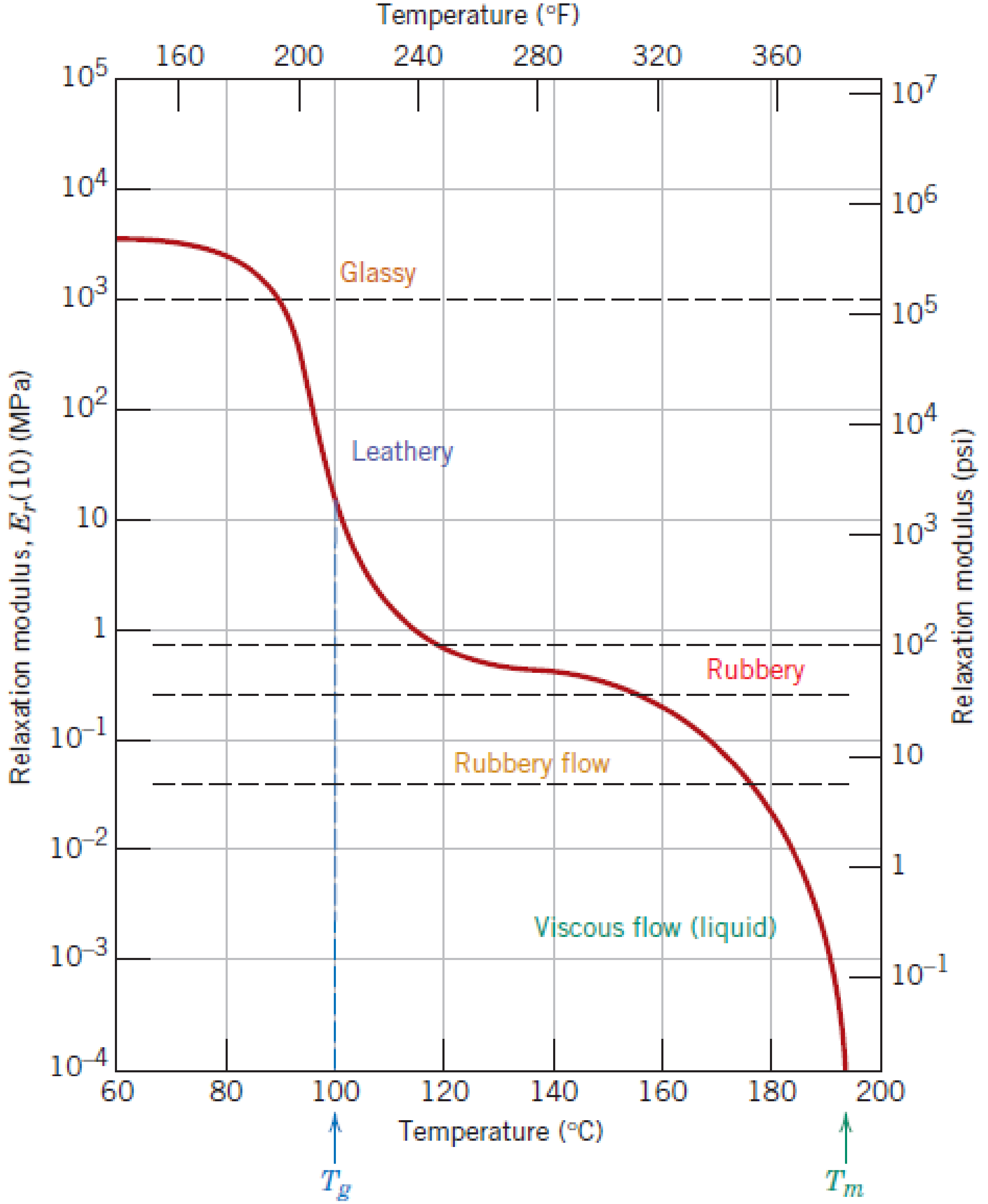
$$E_r(t) = \frac{\sigma(t)}{\varepsilon_o}$$

- $E_r(t)$ is also a function of temperature.





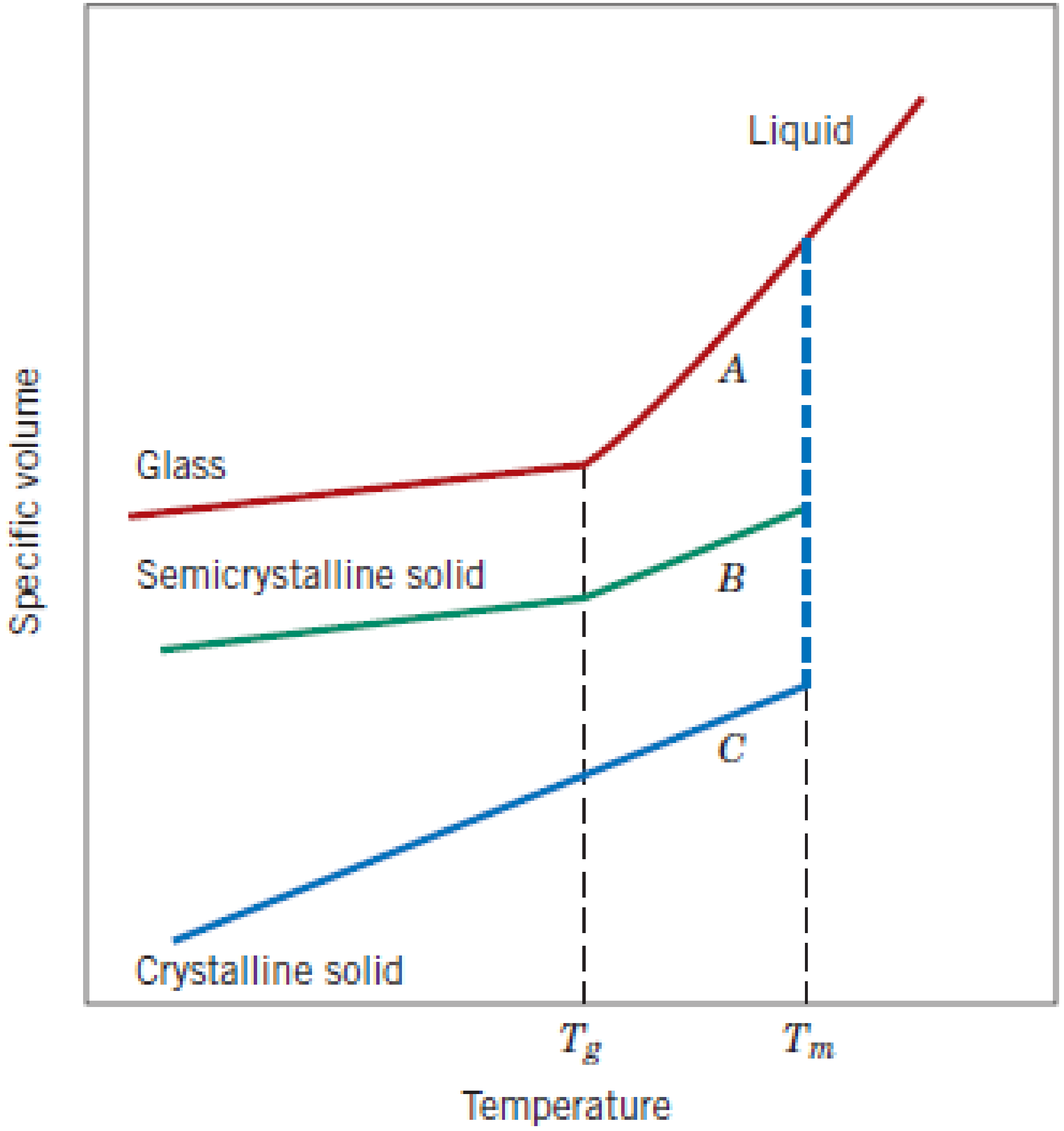
- Relaxation modulus is a function temperature.



Melting and Glass Transition Temperatures

The glass transition occurs in amorphous (or glassy) and semicrystalline polymers, is due to a reduction in motion of large segments of molecular chains with decreasing temperature.

Upon cooling, the glass transition corresponds to the gradual transformation from a liquid into a rubbery material and finally into a rigid solid.
The temperature at which the polymer experiences the transition from rubbery into rigid states is termed the **glass transition temperature,** T_g. T_g lies between 0.5 – 0.8 T_m



Viscoelastic Creep

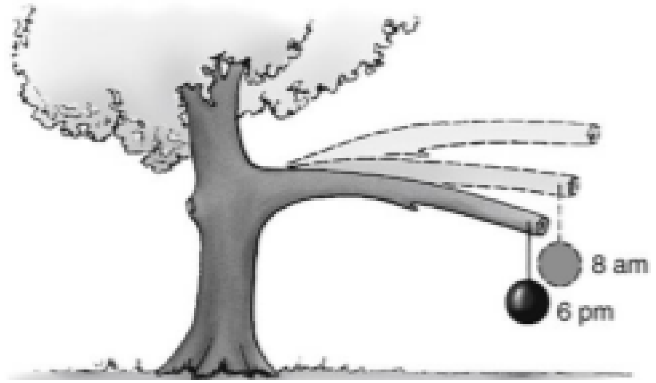
• Many polymers susceptible to time-dependent deformation under constant load – viscoelastic creep.

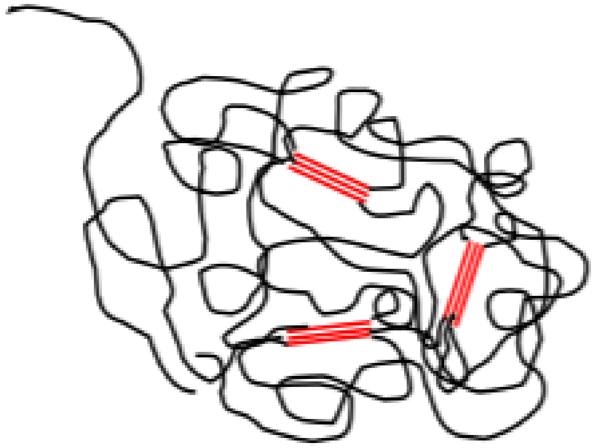
• Creep may be significant even at room temperature and under moderately low stresses (below yield strength).

• Results of creep tests are described by time dependent creep modulus:

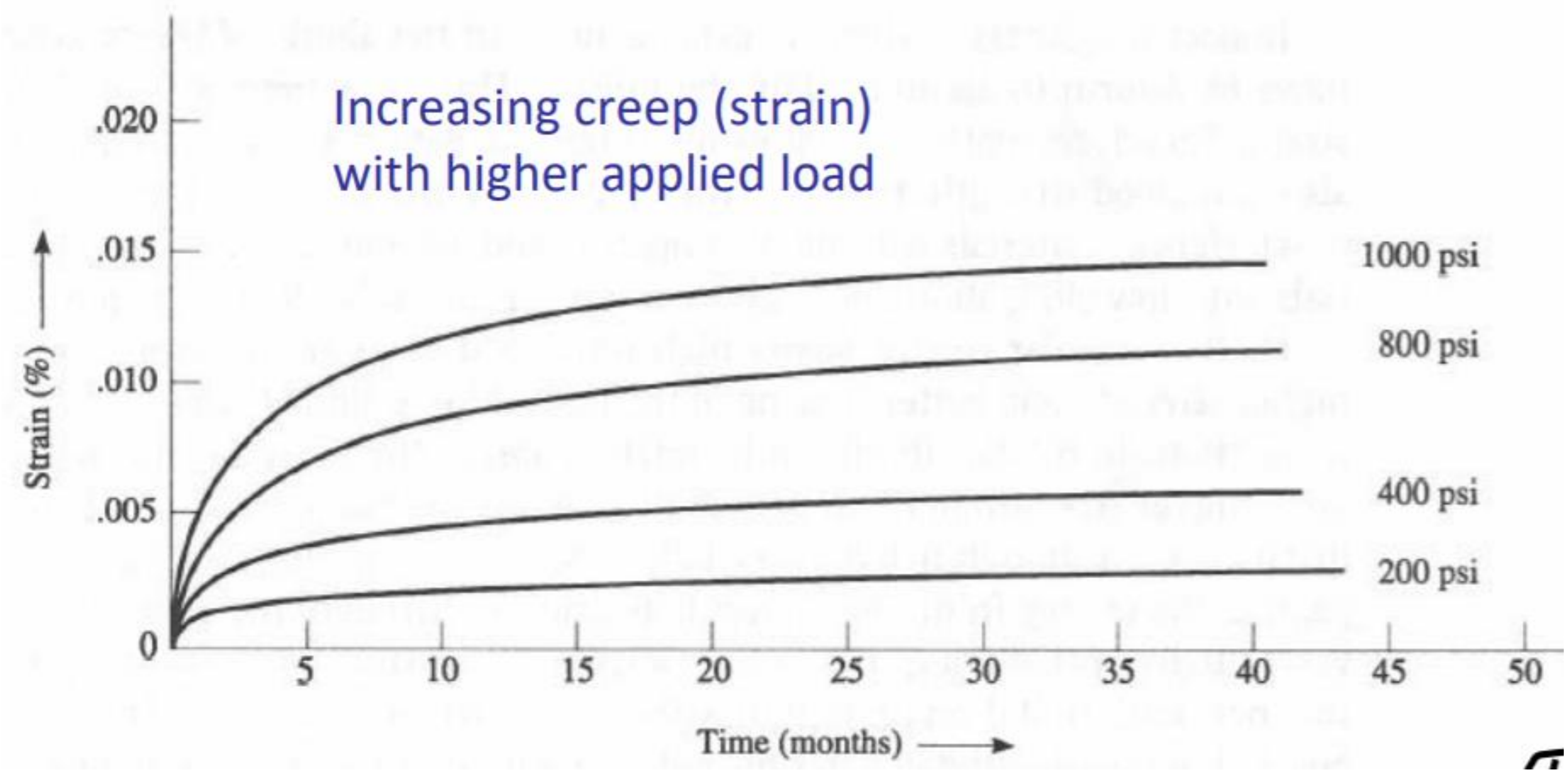
$$E_c(t) = \sigma_o / \varepsilon (t)$$

• Amount of creep decreases as crystallinity increases.





Crystals act like crosslinks


Increasing creep (strain)
with higher applied load
.020
.015
.010
.005
0
Strain (%)
1000 psi
800 psi
400 psi
200 psi
5
10
15
20
25
30
35
40
45
50
Time (months)

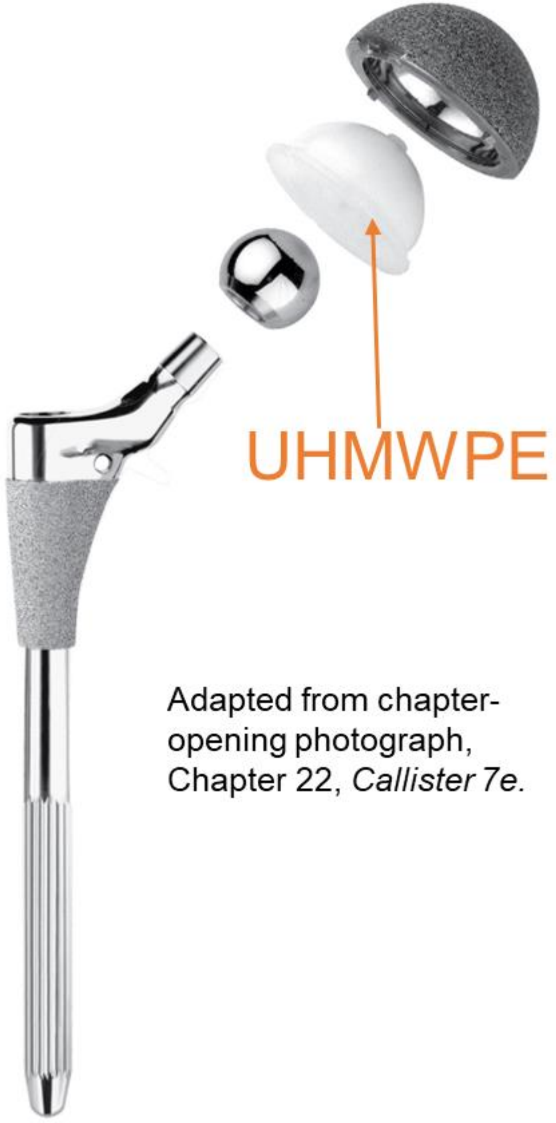
Advanced Polymers

Ultrahigh Molecular Weight Polyethylene (UHMWPE)

- Molecular weight > 4×10^6 g/mol.
- Spectra
- Outstanding properties
  - high impact strength
  - resistance to wear/abrasion
  - low coefficient of friction
  - self-lubricating surface

- Important applications
  - bullet-proof vests
  - golf ball cores
  - hip implants (acetabular cup) –Excellent Biomedical properties

- Disadvantages
  - Has a relatively low melting temperature, mechanical properties deteriorate rapidly with increasing temperature.

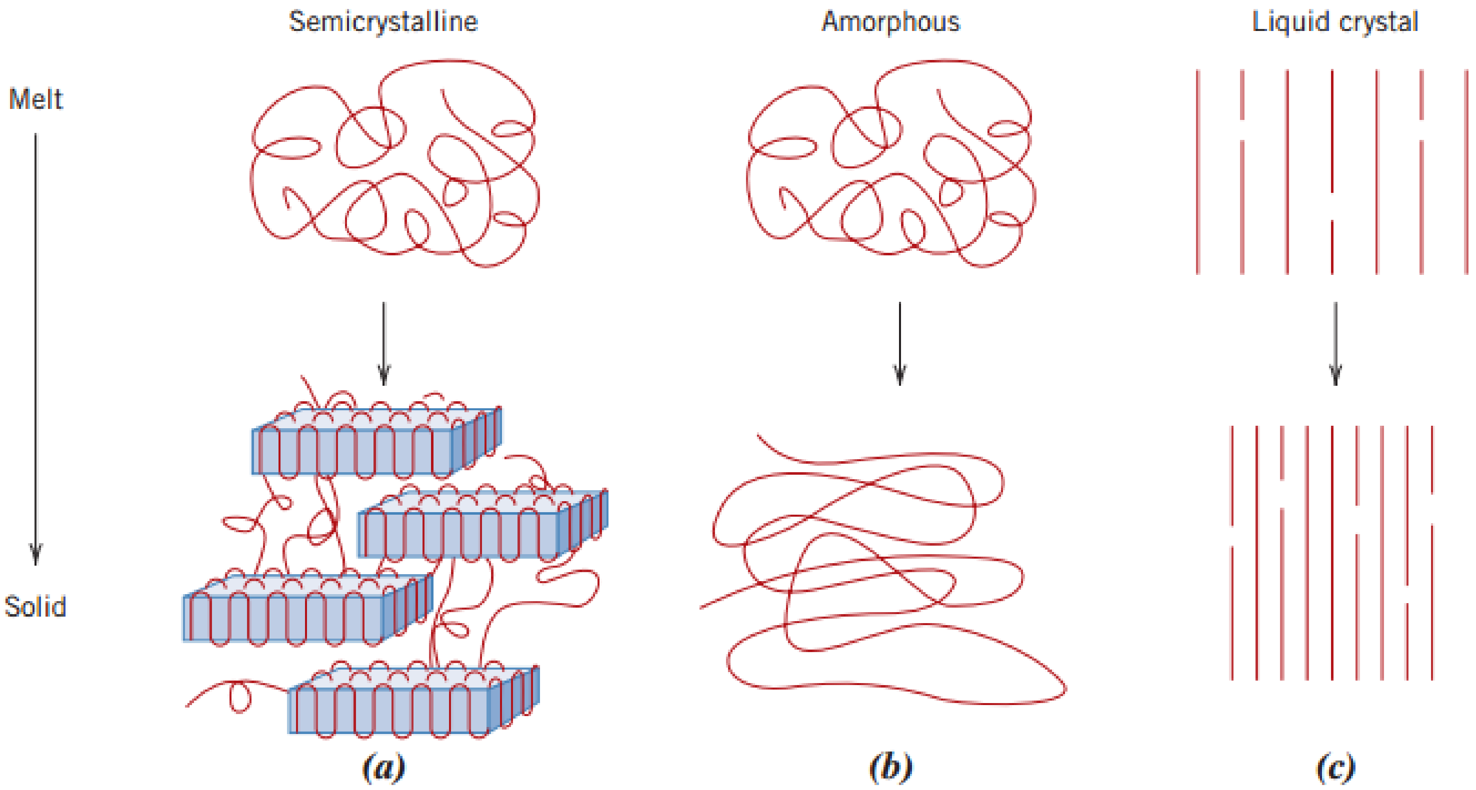


Adapted from chapter-opening photograph, Chapter 22, *Callister 7e.*

Advanced Polymers

Liquid Crystal Polymers (LCPs)

- Chemically complex, structurally distinct.
- Have extended, rod shaped, aligned, rigid molecules.
- Fall under liquid crystalline category.
- Smectic, nematic. Cholesteric are three types.
- Applications
    - Interconnect devices, relays, capacitor housing, LCDs
    - Medical equipment industry
    - Photocopier and fibre-optic components.

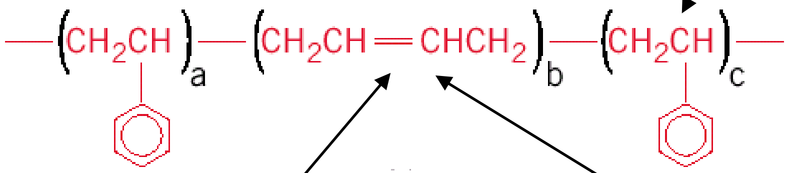


Thermoplastic Elastomers

Styrene-butadiene block copolymer

styrene

hard component domain



butadiene

soft component domain

Fig. 15.21(a), *Callister & Rethwisch 8e.*

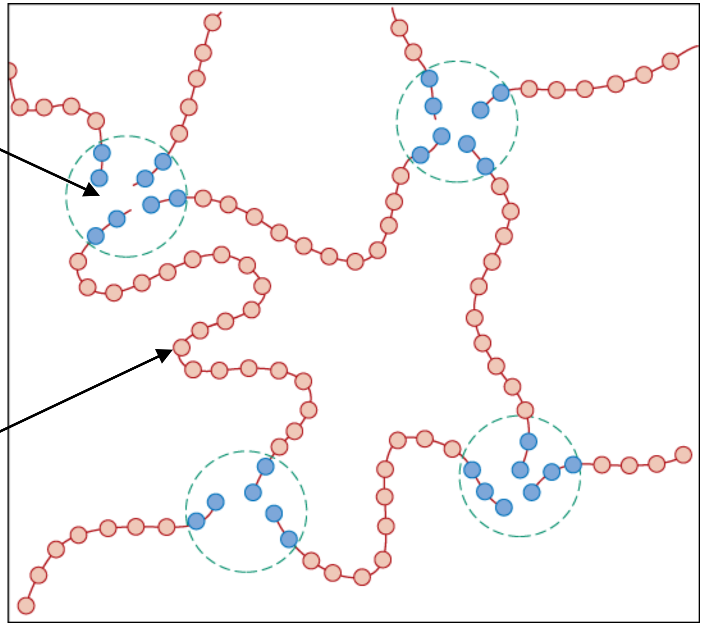
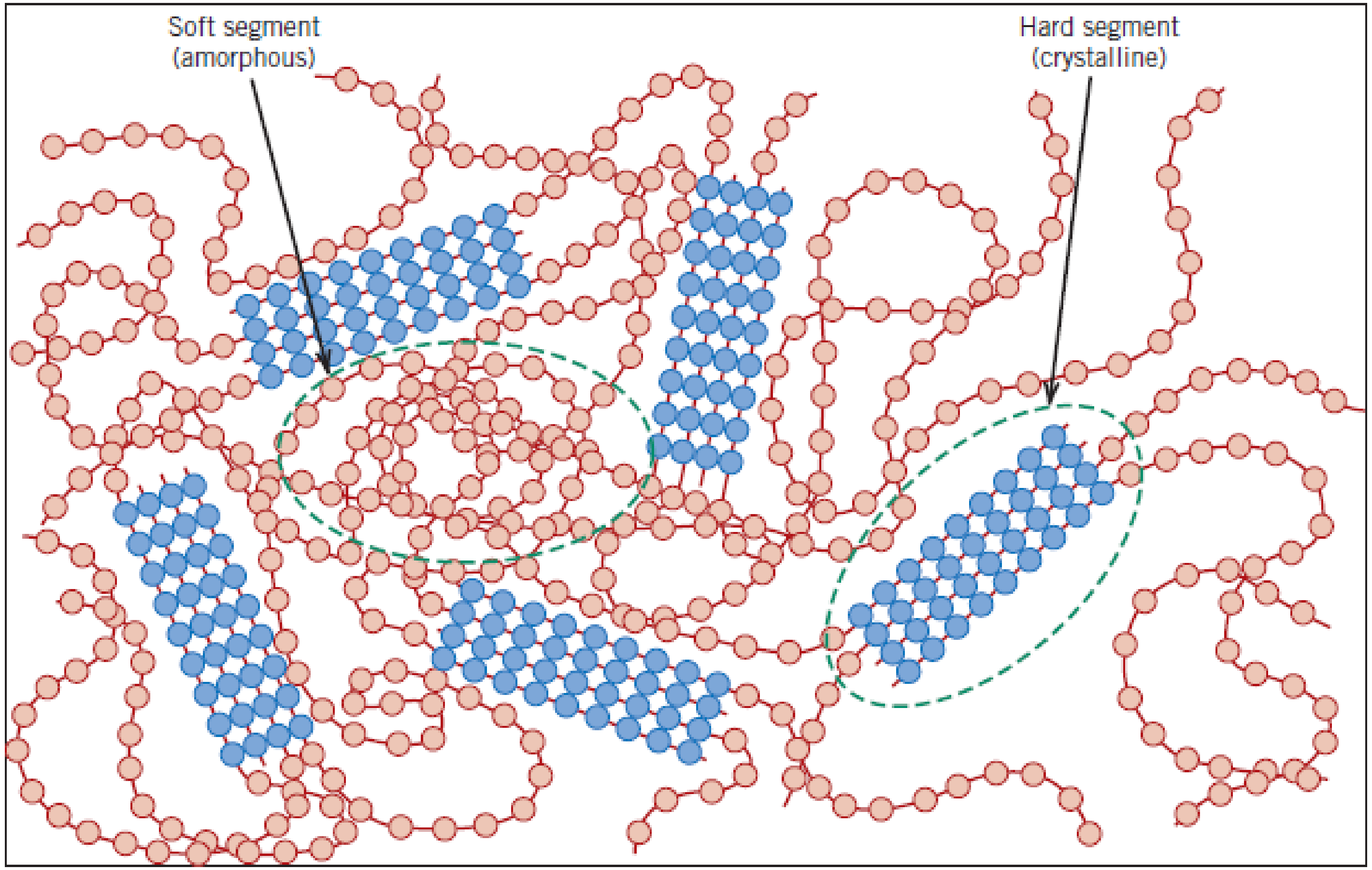


Fig. 15.22, *Callister & Rethwisch 8e.* (Fig. 15.22 adapted from *the Science and Engineering of Materials*, 5th Ed., D.R. Askeland and P.P. Phule, Thomson Learning, 2006.)

The chief advantage of the TPEs over the thermoset elastomers is that upon heating above *Tm* of the hard phase, they melt (i.e., the physical crosslinks disappear), and, therefore it is processed by conventional thermoplastic forming techniques



Thermoplastic elastomers are recyclable; thermoset elastomers are, to a large degree, nonrecyclable.

Scrap generated during forming procedures may also be recycled, which results in lower production costs than with thermosets.

Typical uses for TPEs include

- automotive components (electrical insulation and connectors, and gaskets),
- shoe soles and heels, sporting goods (e.g., bladders for footballs and soccer balls),
- medical barrier films and protective coatings, and
- components in sealants, caulking, and adhesives.