UMP OPEN COURSEWARE

Universiti Malaysia PAHANG
Engineering • Technology • Creativity

BFF1113
Engineering Materials

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Engineering • Technology • Creativity

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FACULTY OF MANUFACTURING ENGINEERING

Course Guidelines:

1. Introduction to Engineering Materials
2. Bonding and Properties
3. Crystal Structures & Properties
4. Imperfection in Solids
5. Mechanical Properties of Materials
6. Physical Properties of Materials
7. Failure & Fundamental of Fracture
8. Metal Alloys
9. Phase Diagram
10. Phase Transformation – Heat Treatment
11. Processing and Application of Metals
12. Ceramic Materials
13. **Polymer Materials**
14. Composite Materials
15. Corrosion & Degradation of Materials
16. Environment and Sustainability

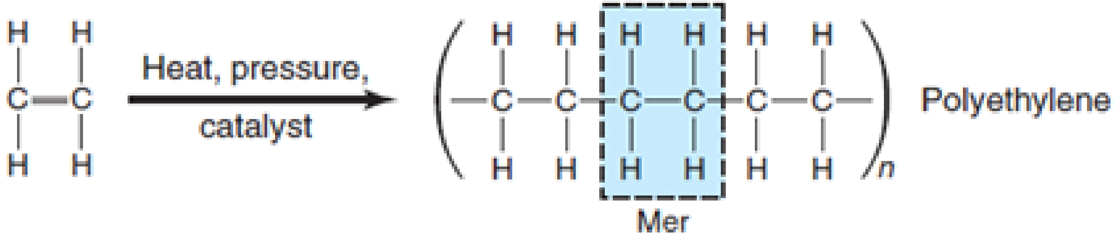
Polymers

Chapter Outline

1. Introduction
2. Thermoplastics, Thermosetting, Elastomer Polymers (Rubbers)
3. The Structure of Polymers
4. General Properties & Application of Polymers
5. Fabrication of Polymer

WHAT YOU SHOULD KNOW…

- **Plastics** is a synonym for **polymers**
- They have large molecules (*macromolecules* or *giant molecules)*
- **Mer** is the smallest repetitive unit
- Polymers are **long-chain molecules** that are formed by ***polymerization -*** Monomers linked into polymers in repeating units



- Advantages of polymers: low cost, corrosion resistance, low electrical and thermal conductivity, low density, high strength-to-weight ratio, noise reduction and ease of manufacturing

1.0: Introduction

POLYMER

The terms **polymer** and **monomer** were derived from the Greek roots poly (many), mono (one) and meros (part).

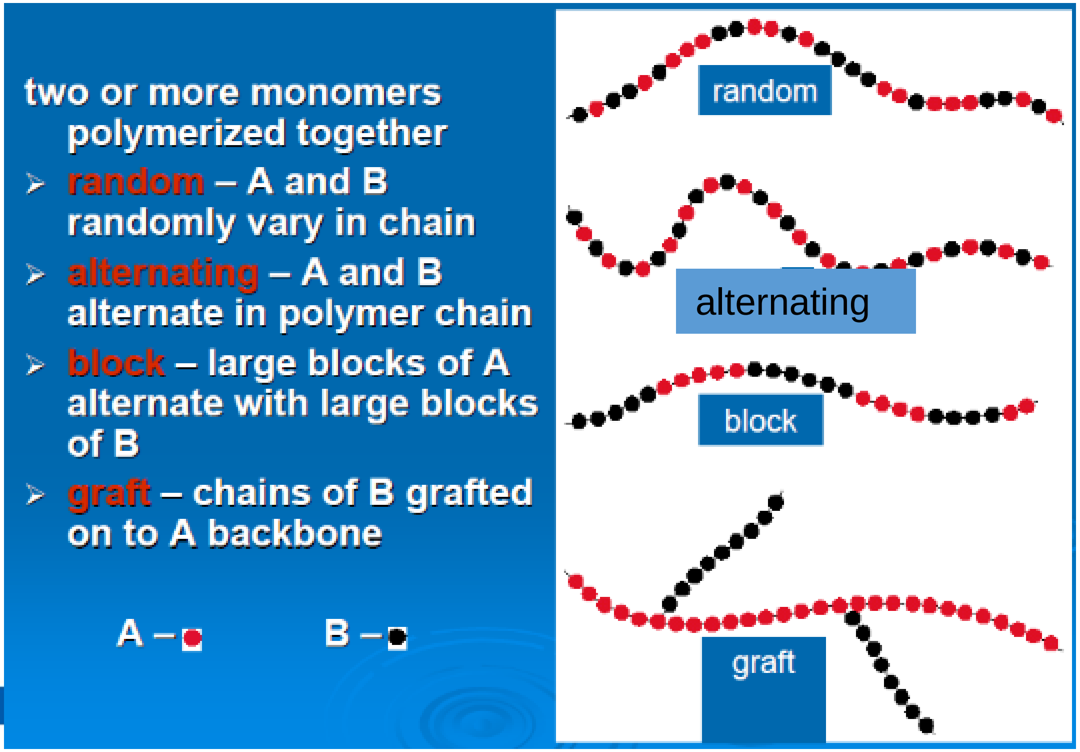
Recognition that polymeric macromolecules make up many important natural materials was followed by the creation of synthetic analogs having a variety of properties.

Indeed, applications of these materials as fibers, flexible films, adhesives, resistant paints and tough but light solids have transformed modern society. Some important examples of these substances are discussed in the following sections.

Copolymers and Terpolymers

- Repeating units in a polymer chain are all of the same type is called a *homopolymer*
- *Copolymers* contain two types of polymers
- *Terpolymers* contain three types

copolymer →



two or more monomers polymerized together

- **random** – A and B randomly vary in chain
- **alternating** – A and B alternate in polymer chain
- **block** – large blocks of A alternate with large blocks of B
- **graft** – chains of B grafted on to A backbone

A – 🔴   B – ●

2.0: CLASS OF POLYMERS

Thermoplastics

- Soften when heated (eventually liquefy)
- Harden when cooled
- Reversible processes and may be repeated (heating/cooling)
- Examples (Polypropylene, Polyethylene)

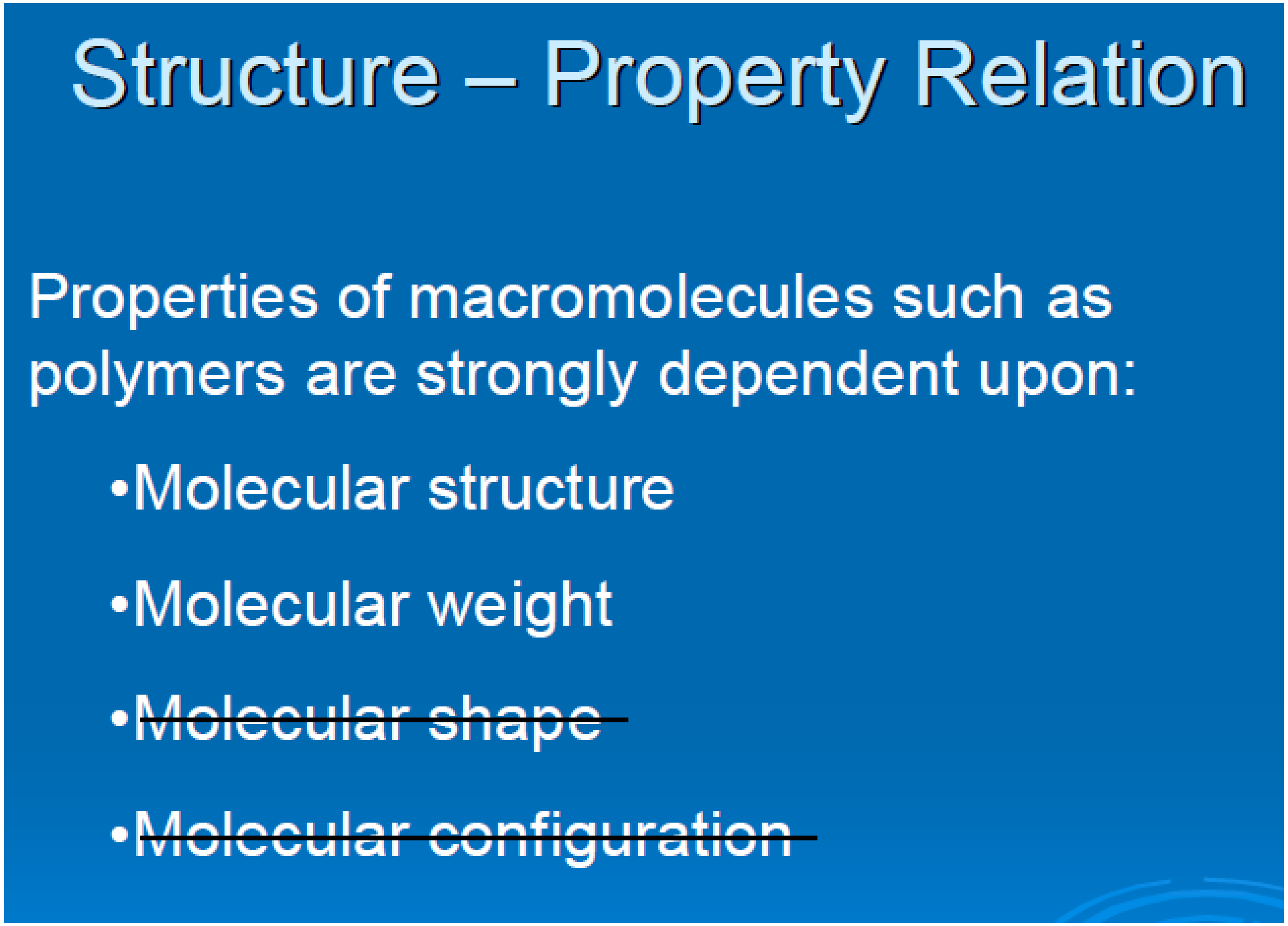
Thermosetting

- Network polymers (cross-linking)
- Permanently hard after formation
- Non-reversible processes (heating/cooling)
- Examples (Epoxy)

Elastomers (Rubbers)

- Elastomers consist of amorphous polymers having a low glass-transition temperature
- They undergo large elastic deformations without rupture
- They are soft and have a low elastic modulus
- They stretch but return to their original shape after the load is removed

3.0: The Structure of Polymers



Structure – Property Relation

Properties of macromolecules such as polymers are strongly dependent upon:

- Molecular structure
- Molecular weight
- ~~Molecular shape~~
- ~~Molecular configuration~~

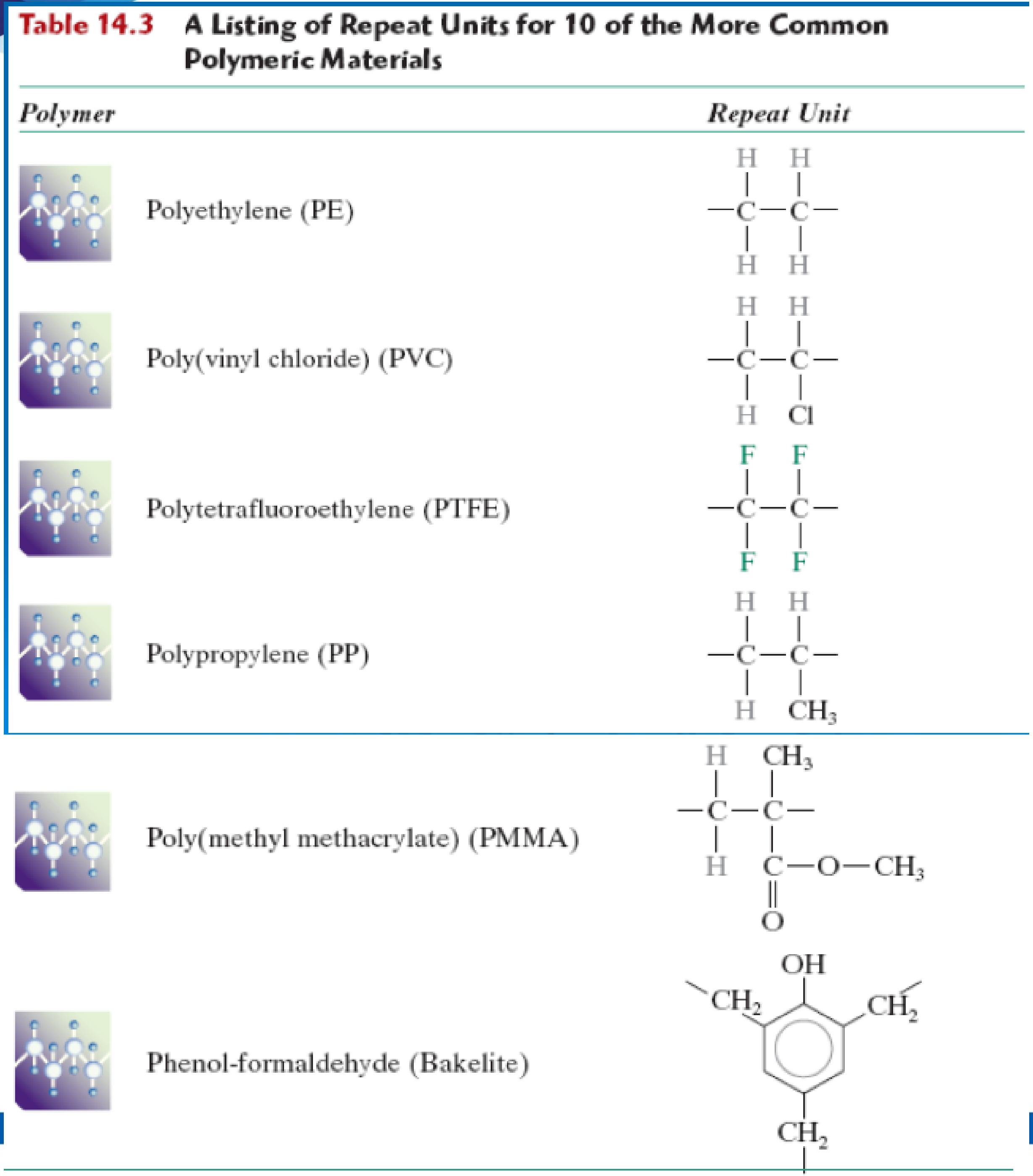
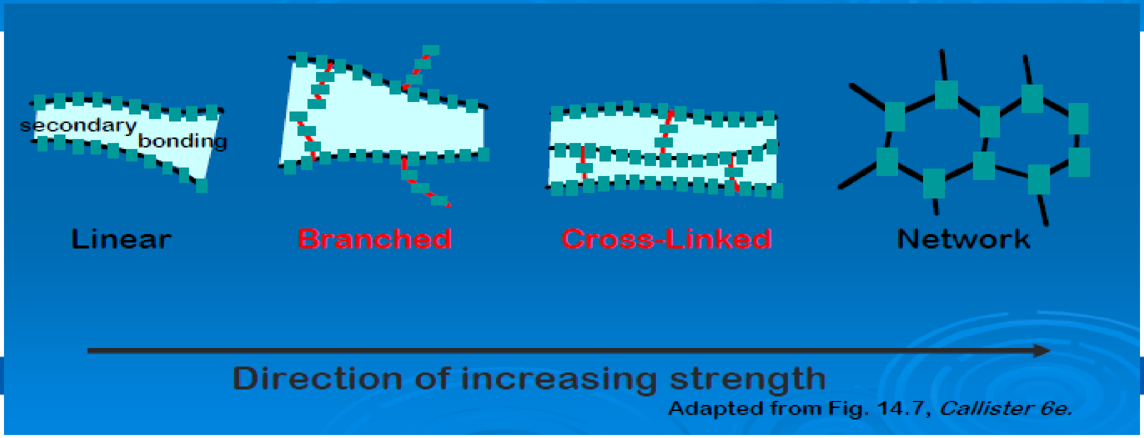


Table 14.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials

Polymer	*Repeat Unit*
Polyethylene (PE)	$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$
Poly(vinyl chloride) (PVC)	$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-$
Polytetrafluoroethylene (PTFE)	$-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-$
Polypropylene (PP)	$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CH_3}{C}}-$
Poly(methyl methacrylate) (PMMA)	$-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{\underset{O}{\overset{\Vert}{C}}-O-CH_3}{C}}-$
Phenol-formaldehyde (Bakelite)	

MOLECULAR STRUCTURE

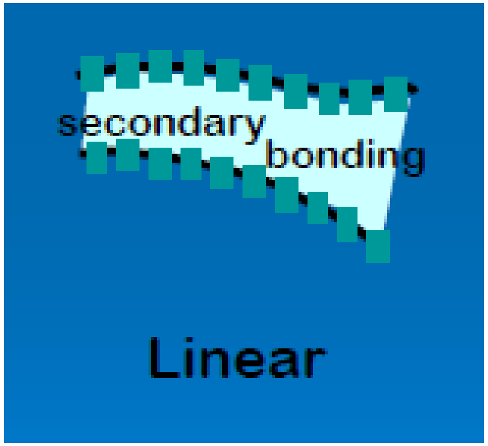
- The molecules in polymer are gigantic and therefore are often referred to as macromolecules
- As a result of being macromolecules, the molecular structure of which polymer are made of could be several such as:
  - Linear
  - Branched
  - Crosslinked
  - Network

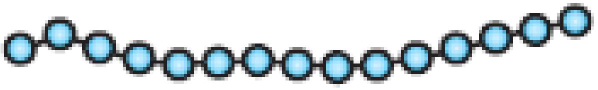


Adapted from Fig. 14.7, *Callister 6e.*

Linear Polymers

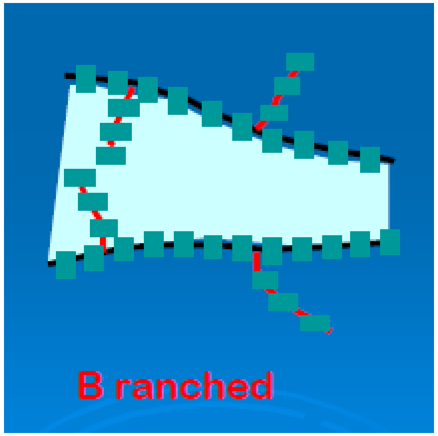
- Chainlike polymers are called *linear polymers* to sequential structure
- Are those in which the repeat unit are joined together end to end in single chain
- May have extensive van derWaals and hydrogen bonding between the chains

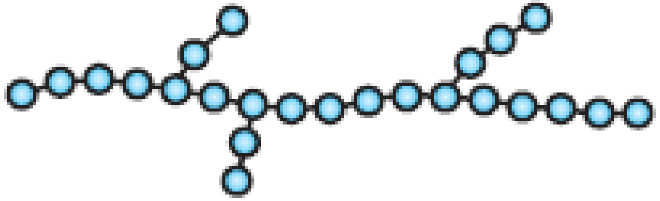



(a) Linear

Branched Polymers

- Are those in which the side-branch chains are connected to the main chain
- The branches may result from side reactions that occur during the synthesis of polymer

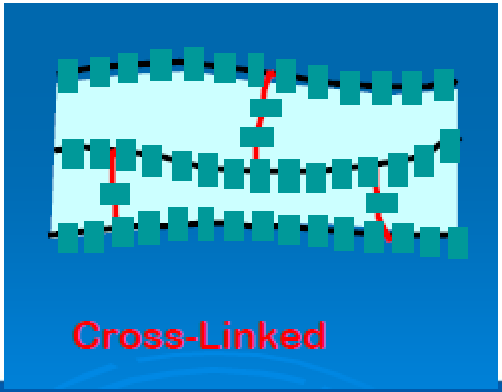


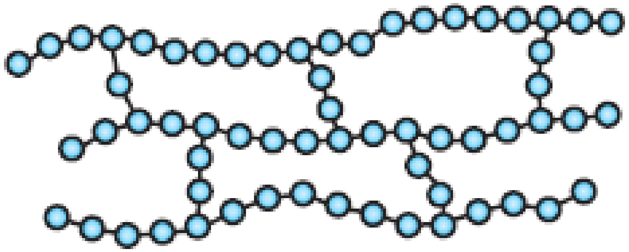


(b) Branched

Cross-linked Polymers

- Are those in which the adjacent linear chains are joined one to anther at various positions by covalent bond
- The process of crosslinking is achieved either during synthesis or by a non-reversible chemical reaction
- Polymers with a cross-linked structure are called **thermosets** or **thermosetting plastics**

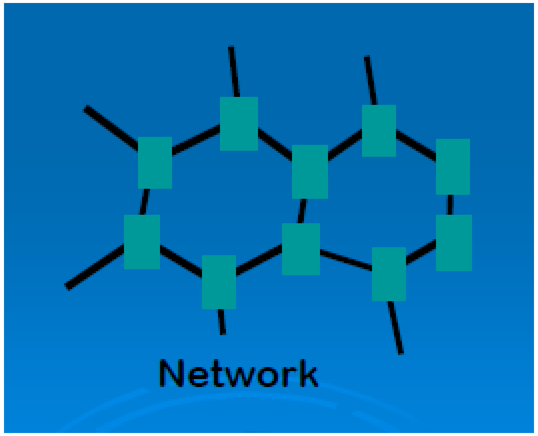


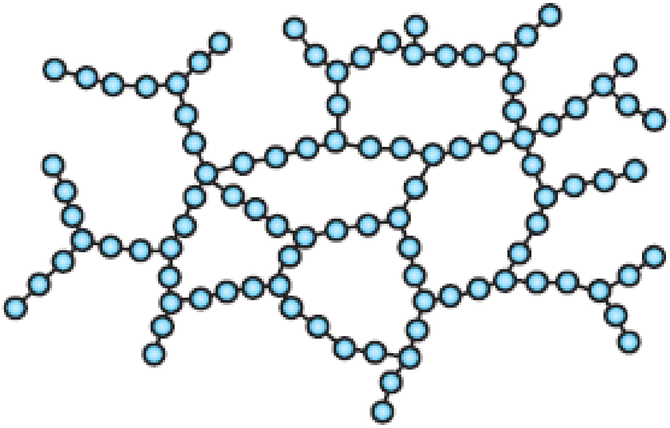


(c) Cross-linked

Network Polymers

- Are those in which the chains are connected in three dimensional networks by covalent bond
- Polymer that is highly crosslinked which are regarded as a network polymer

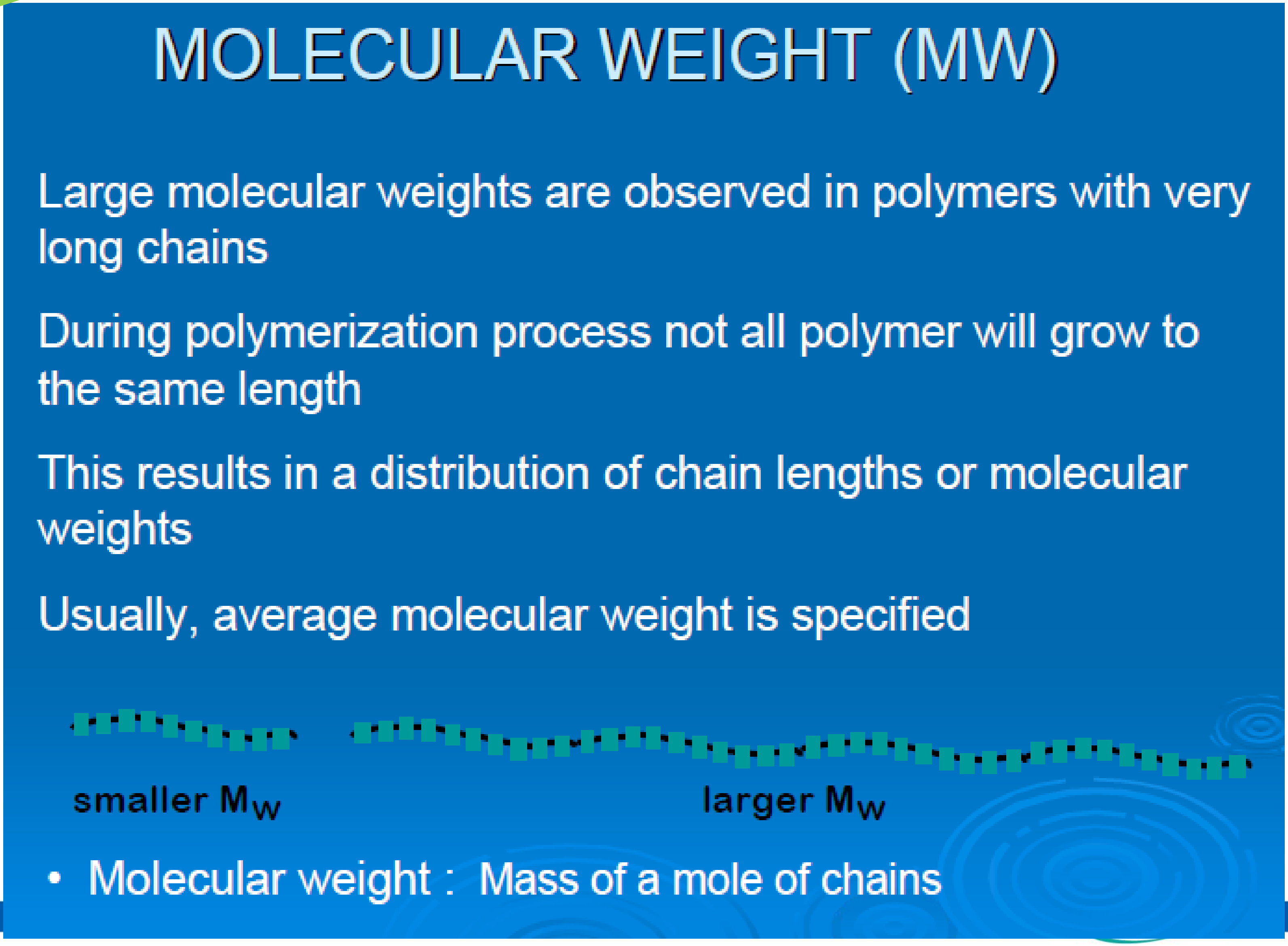




(d) Network

MOLECULAR WEIGHT

Higher the molecular weight of a given polymer, the greater the average chain length



MOLECULAR WEIGHT (MW)

Large molecular weights are observed in polymers with very long chains

During polymerization process not all polymer will grow to the same length

This results in a distribution of chain lengths or molecular weights

Usually, average molecular weight is specified

smaller M_w

larger M_w

- Molecular weight : Mass of a mole of chains

Effect of molecular weight on properties of polymers

Molecular weight has a strong effect on the properties of the polymers

High molecular weight means the polymer is relatively stronger than the low molecular weight one due to the longer chain which tends to entangle together. Typical example is the tensile strength and tensile modulus and thermal properties

MOLECULAR SHAPE

Molecular shape of Polymers

- Related to the arrangement of atom in backbone of polymer chain

- Single chain bond are capable of rotating and bending in three dimensions (i.e. zig-zag etc)

- This leads to extensive intertwining and entanglement of neighbouring chain molecules, a situation similar to a heavily tangled fishing line.

- These random coils and molecular entanglements are responsible for a number of important characteristics of polymers, to include the large elastic extensions displayed by the rubber materials

- Some of the mechanical and thermal characterisitcs of polymers are a function of the ability of chain segments to experience rotation in response to applied stress and thermal vibrations

C may lie at any point at cone

A straight chain is formed when chain atom positioned in zig zag form

Chain bending and twisting when rotation of the chain atom into other position

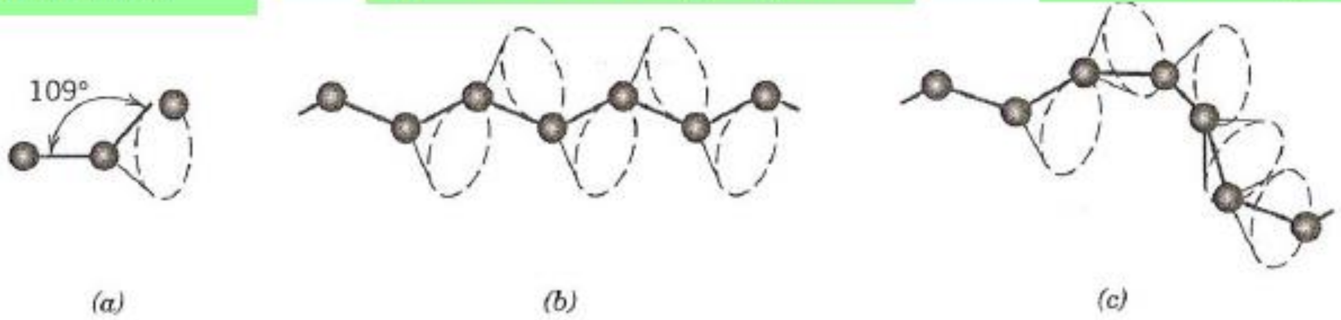


Figure 14.5 Schematic representations of how polymer chain shape is influenced by the positioning of backbone carbon atoms (gray circles). For (*a*), the rightmost atom may lie anywhere on the dashed circle and still subtend a 109° angle with the bond between the other two atoms. Straight and twisted chain segments are generated when the backbone atoms are situated as in (*b*) and (*c*), respectively. (From *Science and Engineering of Materials,* 3rd edition by Askeland. © 1994. Reprinted with permission of Nelson, a division of Thomson Learning: www.thomsonrights.com. Fax 800 730-2215.)

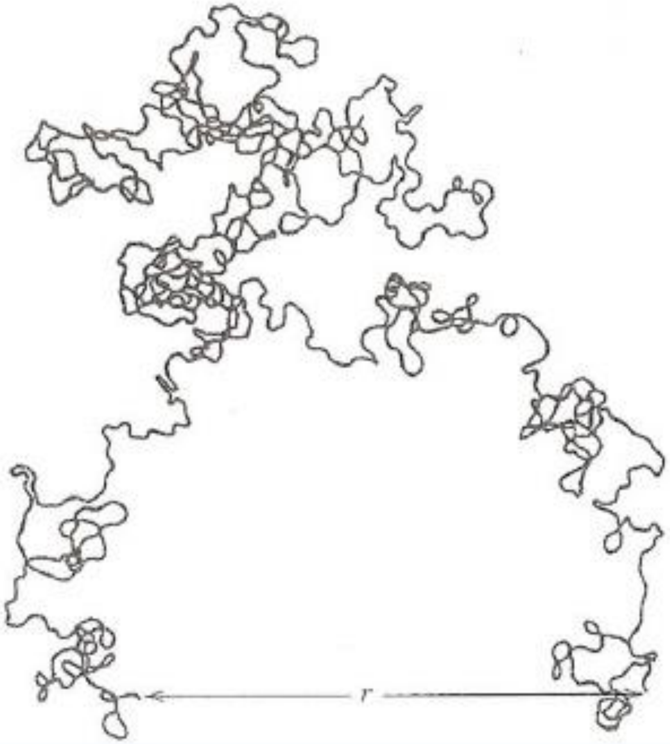
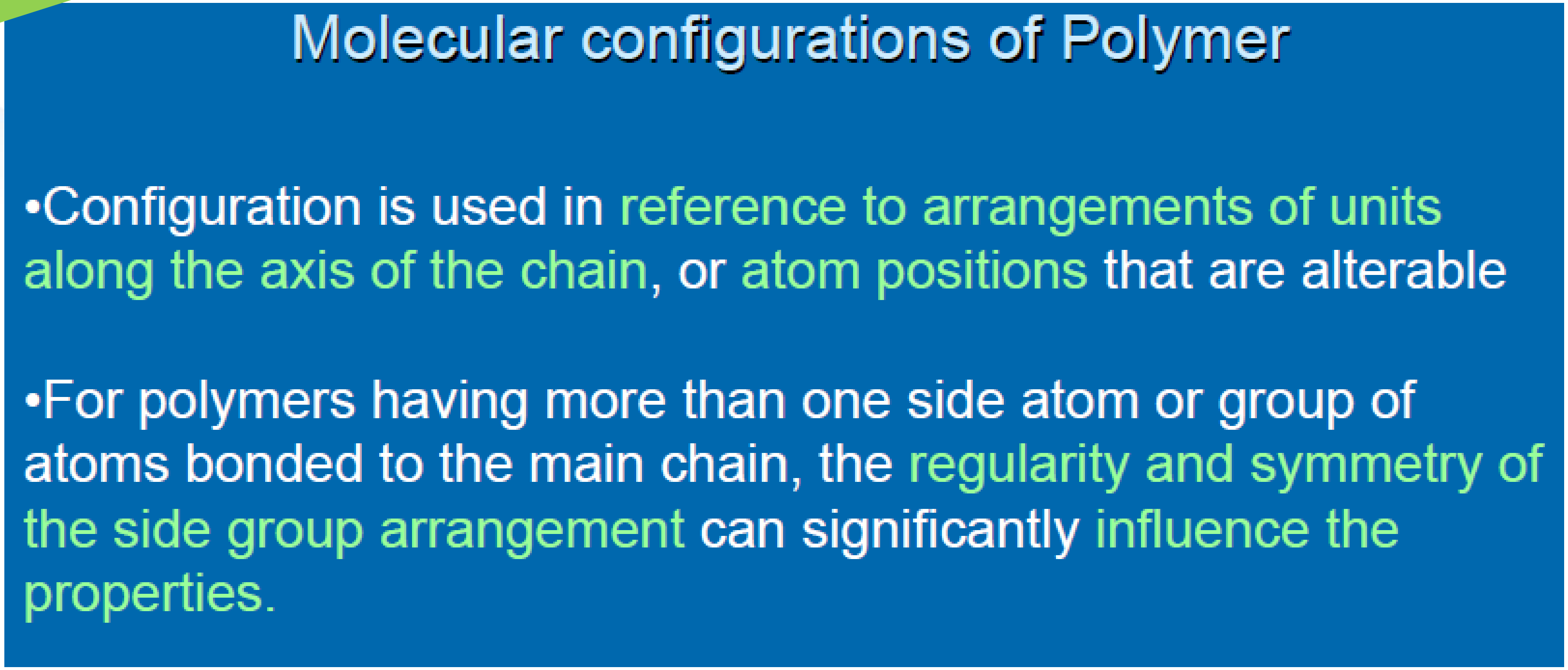


Figure 14.6 Schematic representation of a single polymer chain molecule that has numerous random kinks and coils produced by chain bond rotations. (From L. R. G. Treloar, *The Physics of Rubber Elasticity,* 2nd edition, Oxford University Press, Oxford, 1958, p. 47.)

A single chain molecules composed of many chain atoms-have many bends, twists and kinks

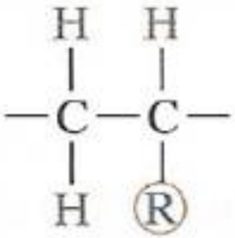
MOLECULAR CONFIGURATION



Molecular configurations of Polymer

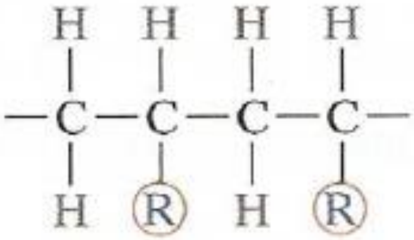
- Configuration is used in reference to arrangements of units along the axis of the chain, or atom positions that are alterable

- For polymers having more than one side atom or group of atoms bonded to the main chain, the regularity and symmetry of the side group arrangement can significantly influence the properties.



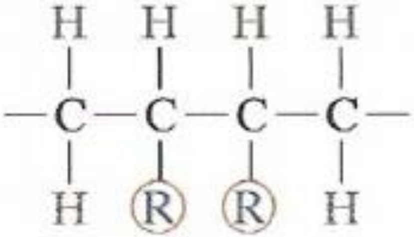
$$\begin{array}{ccccc} & \mathrm{H} & & \mathrm{H} & \\ & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & - \\ & | & & | & \\ & \mathrm{H} & & \mathrm{R} & \end{array}$$

in which R represents an atom or side group other than hydrogen (e.g., Cl, CH_3). One arrangement is possible when the R side groups of successive repeat units are bound to alternate carbon atoms as follows:



$$\begin{array}{ccccccccc} & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \\ & | & & | & & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - \\ & | & & | & & | & & | & \\ & \mathrm{H} & & \mathrm{R} & & \mathrm{H} & & \mathrm{R} & \end{array}$$

This is designated as a head-to-tail configuration.[7] Its complement, the head-to-head configuration, occurs when R groups are bound to adjacent chain atoms:

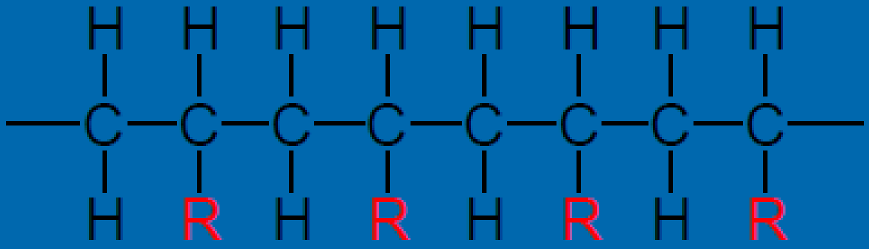


$$\begin{array}{ccccccccc} & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \\ & | & & | & & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - \\ & | & & | & & | & & | & \\ & \mathrm{H} & & \mathrm{R} & & \mathrm{R} & & \mathrm{H} & \end{array}$$

Tacticity

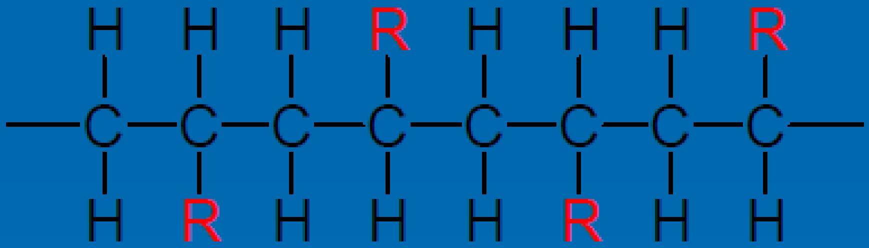
Tacticity – **stereoregularity (stereoisomers) of chain**

isotactic – all R groups on same side of chain



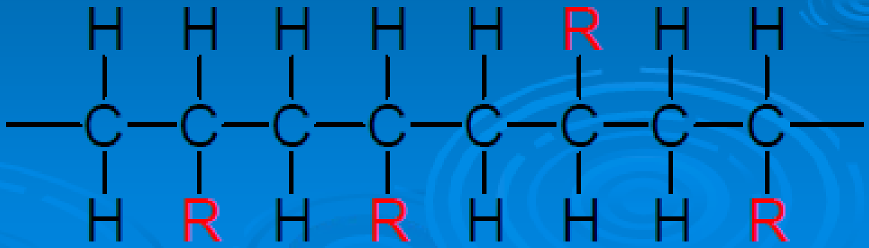
$$\begin{array}{ccccccccccccccccc} & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ & \mathrm{H} & & \mathrm{R} & & \mathrm{H} & & \mathrm{R} & & \mathrm{H} & & \mathrm{R} & & \mathrm{H} & & \mathrm{R} & \end{array}$$

syndiotactic – R groups alternate sides



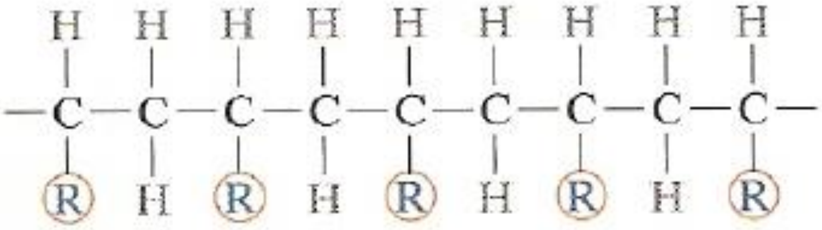
$$\begin{array}{ccccccccccccccccc} & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{R} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{R} & \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ & \mathrm{H} & & \mathrm{R} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{R} & & \mathrm{H} & & \mathrm{H} & \end{array}$$

atactic – R groups random

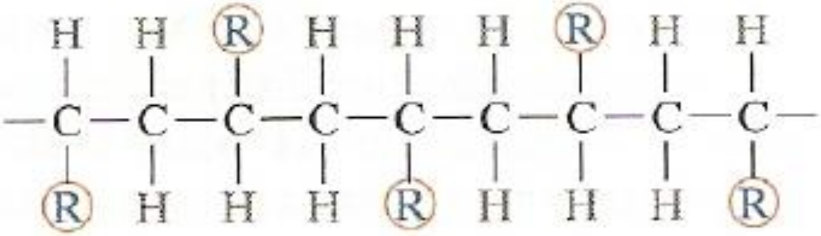


$$\begin{array}{ccccccccccccccccc} & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{R} & & \mathrm{H} & & \mathrm{H} & \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ & \mathrm{H} & & \mathrm{R} & & \mathrm{H} & & \mathrm{R} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{R} & \end{array}$$

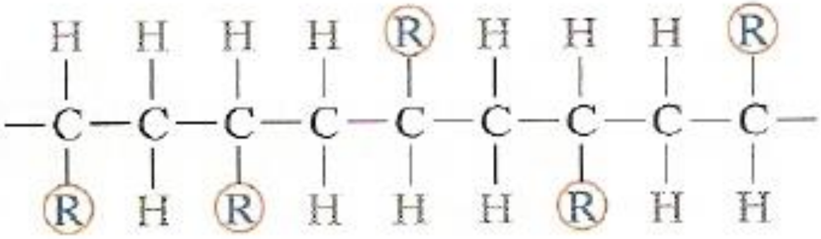
[8] The isotactic configuration is sometimes represented using the following linear (i.e., nonzigzag) and two-dimensional schematic:

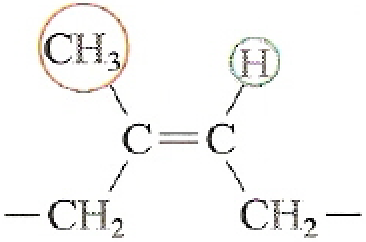


[9] The linear and two-dimensional schematic for syndiotactic is represented as

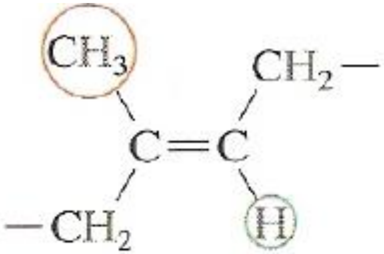


[10] For atactic the linear and two-dimensional schematic is





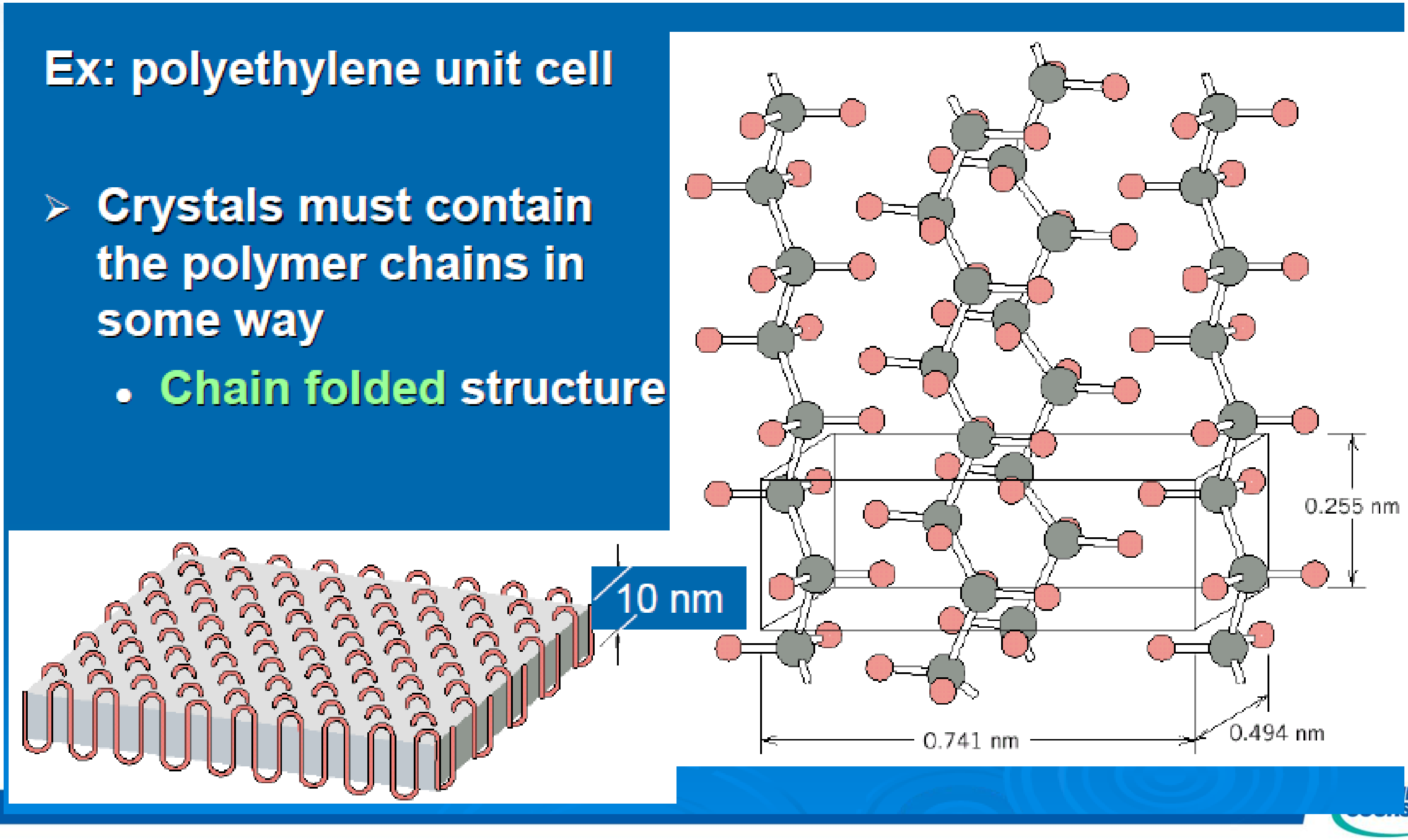
in which the CH_3 group and the H atom are positioned on the same side of the double bond. This is termed a **cis** structure, and the resulting polymer, *cis*-polyisoprene, is natural rubber. For the alternative isomer



the **trans** structure, the CH_3 and H reside on opposite sides of the double bond.[11] *Trans*-polyisoprene, sometimes called gutta percha, has properties that are distinctly different from natural rubber as a result of this configurational alteration. Conversion of trans to cis, or vice versa, is not possible by a simple chain bond rotation because the chain double bond is extremely rigid.

Crystallinity in Polymer

- Crystals are formed when the long molecules arrange themselves in an orderly manner

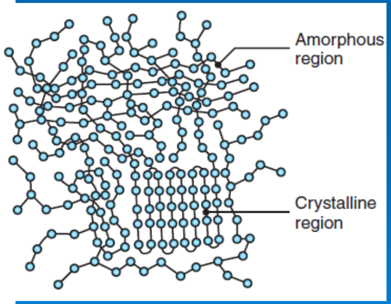


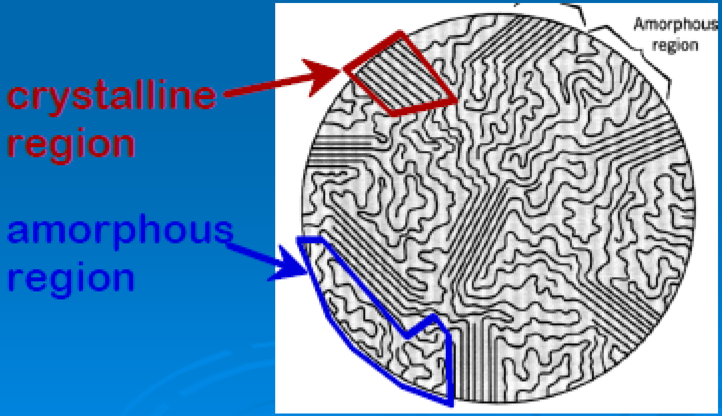
Ex: polyethylene unit cell

- **Crystals must contain the polymer chains in some way**
  - **Chain folded structure**

Effect of crystallinity on properties of semi crystalline polymers

- For semi-crystalline polymers (PP, PE etc) the % of crystallinity affects the properties
- Higher % of crystallinity often results in:
  - Increase in tensile strength
  - Increase in modulus of elasticity
- Annealing causes crystalline regions to grow. Hence, the % of crystallinity increases.



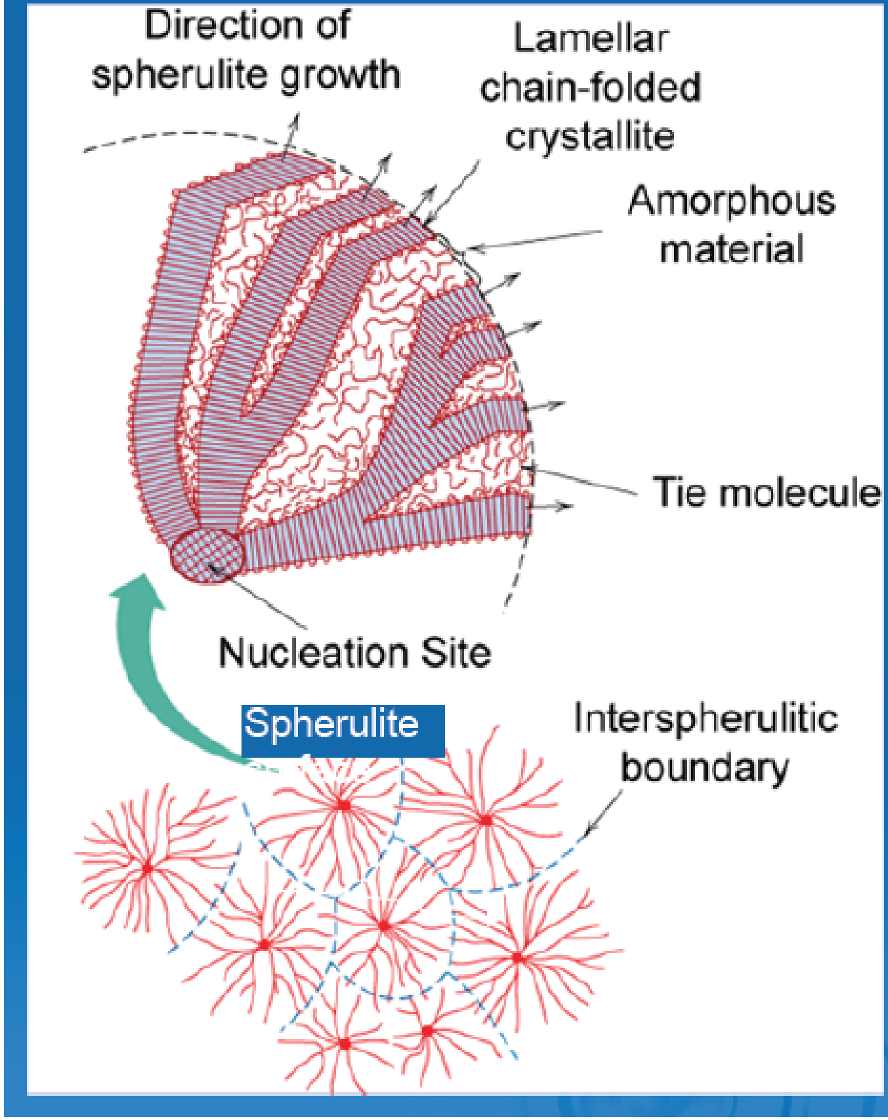

crystalline region

amorphous region

Microstructure of semi-crystalline polymers

- As crystallinity increases, polymers become stiffer, harder, less ductile, more dense, less rubbery, and more resistant to solvents and heat

Polymer Crystal Forms

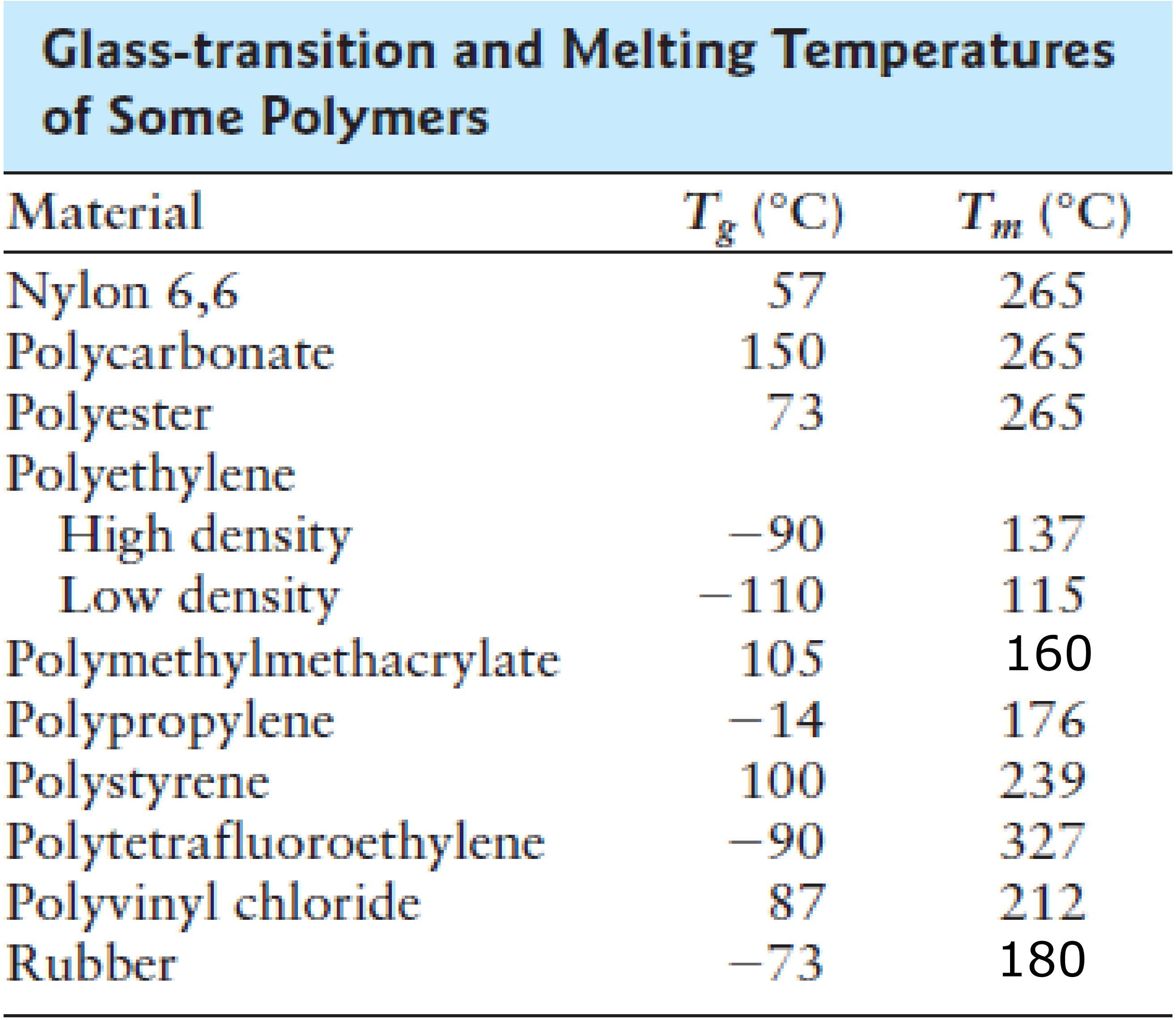


- **Spherulites** – fast growth – forms lamellar (layered) structures
- Ribbon like Chain folded crystallites (lamella) 10nm thick that radiate from a single nucleation site
- Tie chain molecules act as connecting links between adjacent lamella and amorphus region

- At low temperatures, polymer are hard, rigid, brittle, and glassy
- At high temperatures, they are rubbery or leathery

<u>The Terms:</u>

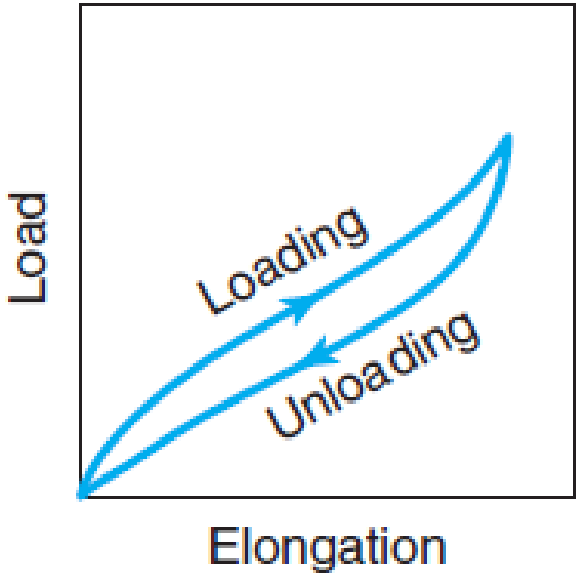
- Melting temperature, T_m
  - Transformation solid (ordered structure) to liquid (highly random)
- The Glass Transition Temp, T_g
  - Transition form rigid to rubbery state.



Glass-transition and Melting Temperatures of Some Polymers

Material	T_g (°C)	T_m (°C)
Nylon 6,6	57	265
Polycarbonate	150	265
Polyester	73	265
Polyethylene		
High density	−90	137
Low density	−110	115
Polymethylmethacrylate	105	160
Polypropylene	−14	176
Polystyrene	100	239
Polytetrafluoroethylene	−90	327
Polyvinyl chloride	87	212
Rubber	−73	180

- **Elastomer** is capable of recovering substantially in shape and size after the load has been removed
- A **rubber** is capable of recovering from large deformations quickly
- Hardness of elastomers increases with the cross-linking of the molecular chains



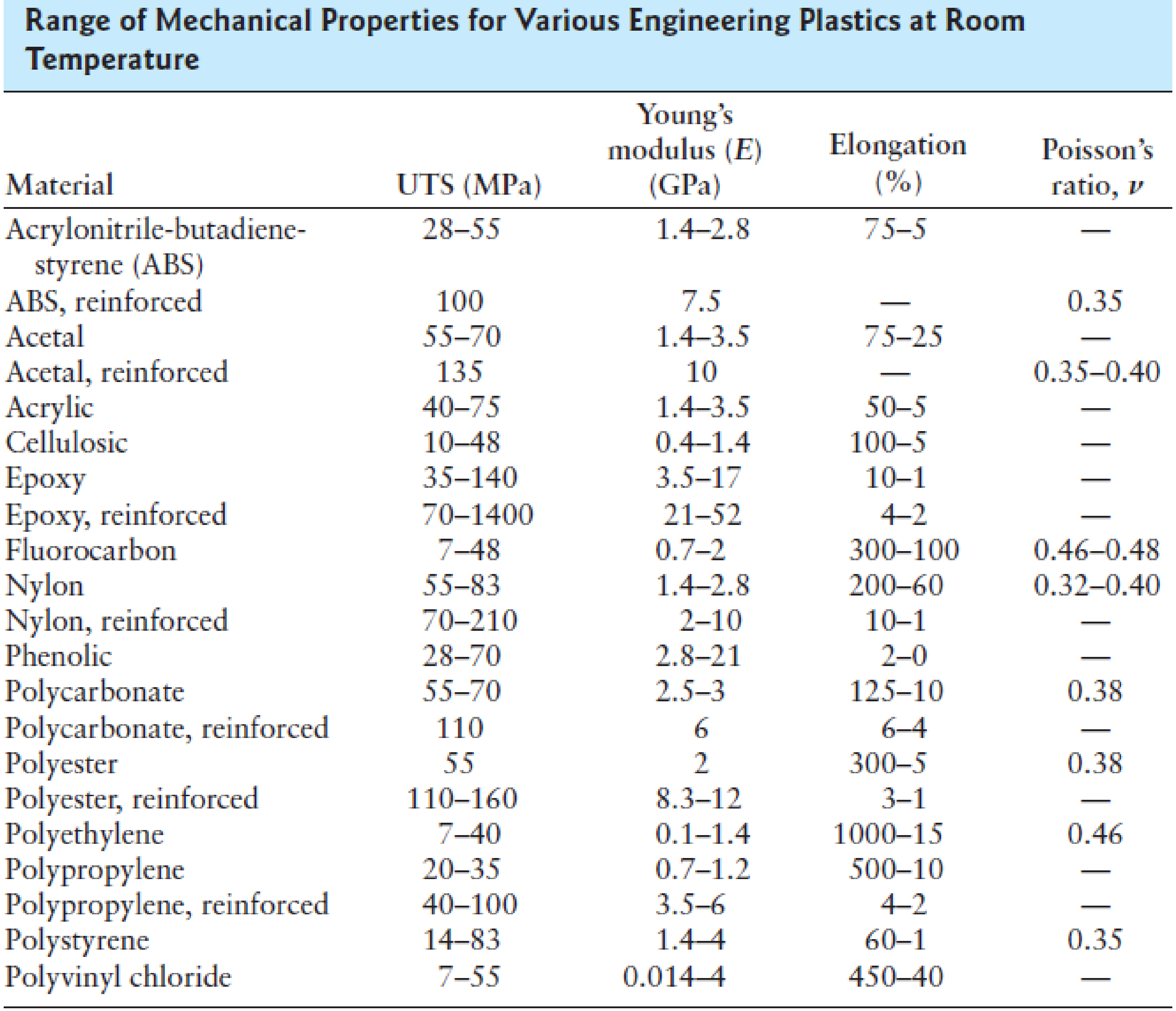
Natural Rubber

- Base for natural rubber is **latex**
- Has good resistance to abrasion and fatigue, and high friction, low resistance, to oil, heat, ozone, and sunlight

Synthetic Rubbers

- Have better resistance to heat, gasoline, and chemicals, higher range of useful temperatures
- Ex: Polybutadiene rubber

Properties & Application of Polymers



Range of Mechanical Properties for Various Engineering Plastics at Room Temperature

Material	UTS (MPa)	Young's modulus (E) (GPa)	Elongation (%)	Poisson's ratio, ν
Acrylonitrile-butadiene-styrene (ABS)	28–55	1.4–2.8	75–5	—
ABS, reinforced	100	7.5	—	0.35
Acetal	55–70	1.4–3.5	75–25	—
Acetal, reinforced	135	10	—	0.35–0.40
Acrylic	40–75	1.4–3.5	50–5	—
Cellulosic	10–48	0.4–1.4	100–5	—
Epoxy	35–140	3.5–17	10–1	—
Epoxy, reinforced	70–1400	21–52	4–2	—
Fluorocarbon	7–48	0.7–2	300–100	0.46–0.48
Nylon	55–83	1.4–2.8	200–60	0.32–0.40
Nylon, reinforced	70–210	2–10	10–1	—
Phenolic	28–70	2.8–21	2–0	—
Polycarbonate	55–70	2.5–3	125–10	0.38
Polycarbonate, reinforced	110	6	6–4	—
Polyester	55	2	300–5	0.38
Polyester, reinforced	110–160	8.3–12	3–1	—
Polyethylene	7–40	0.1–1.4	1000–15	0.46
Polypropylene	20–35	0.7–1.2	500–10	—
Polypropylene, reinforced	40–100	3.5–6	4–2	—
Polystyrene	14–83	1.4–4	60–1	0.35
Polyvinyl chloride	7–55	0.014–4	450–40	—

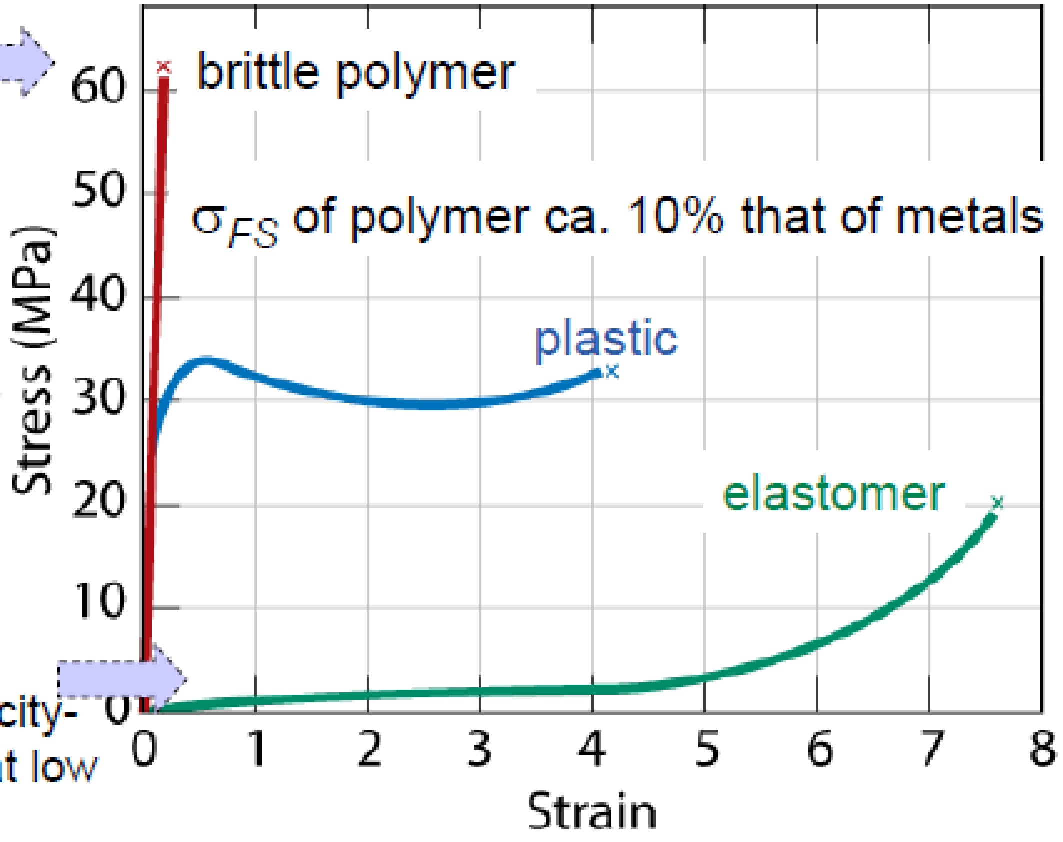
Mechanical **Properties**

- i.e. stress-strain behavior of polymers 3 different stress-starin

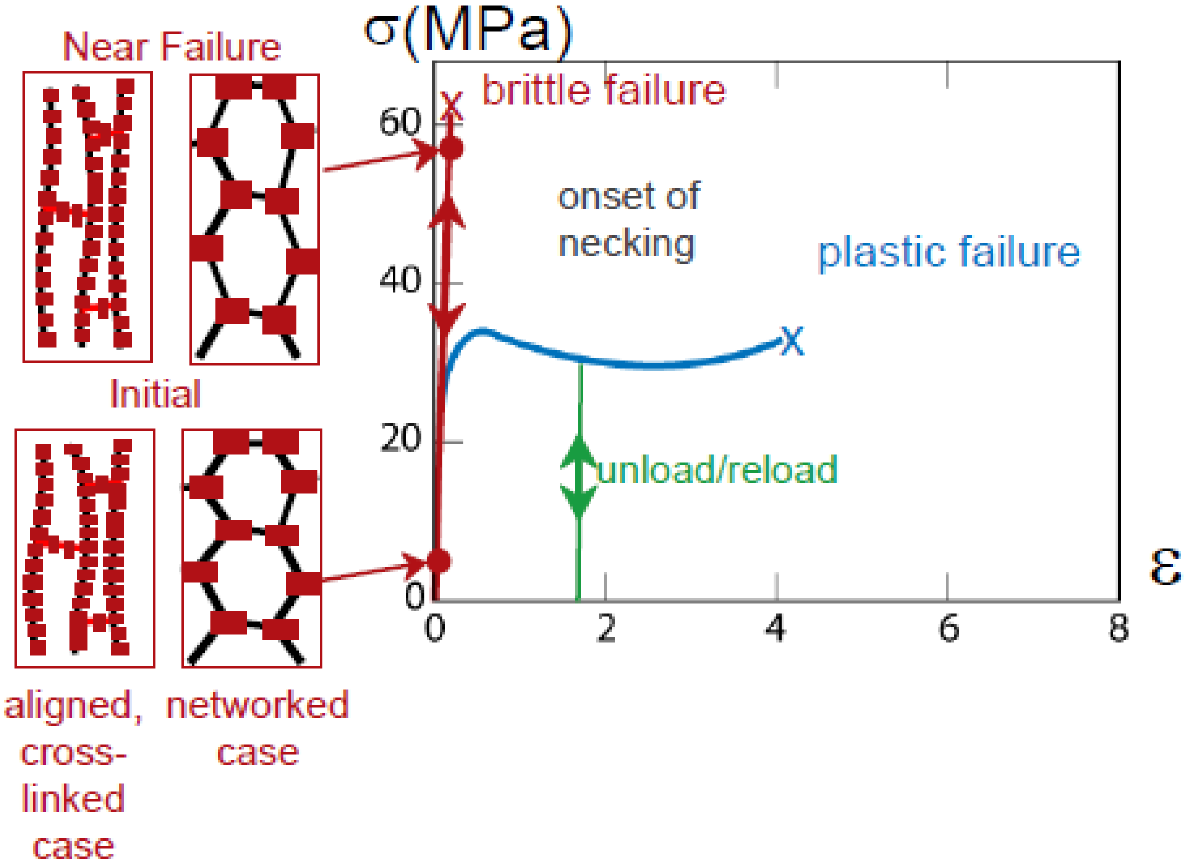
Fracture while deforming elastically

Like metallic materials, initially elastic, followed by yielding and plastic deformation

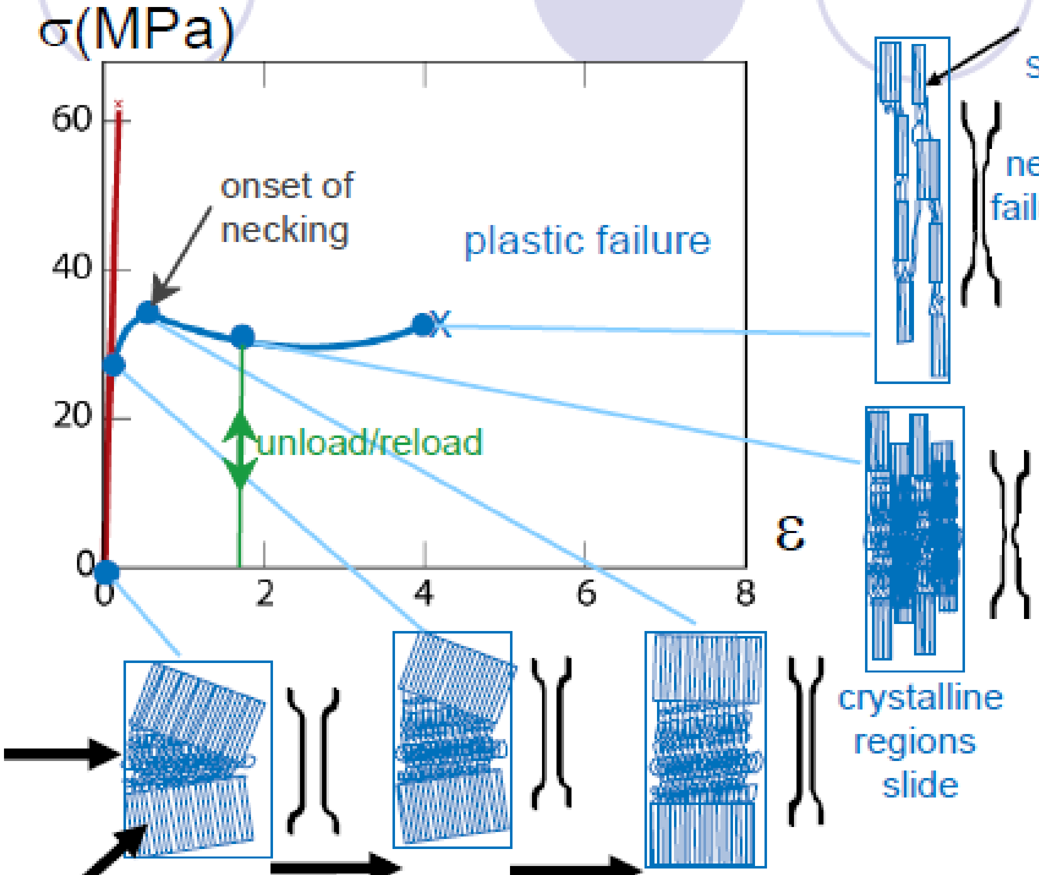
Totally rubber like elasticity- larre recoverable stain at low stress rate



Tensile Response: Brittle Failure



Semicrystalline- Elastic and plastic deformation



Orientation of block segments and tie chain with the tensile axis

Separation of crystalline block segment

crystalline regions slide

Interlamella amorphous region

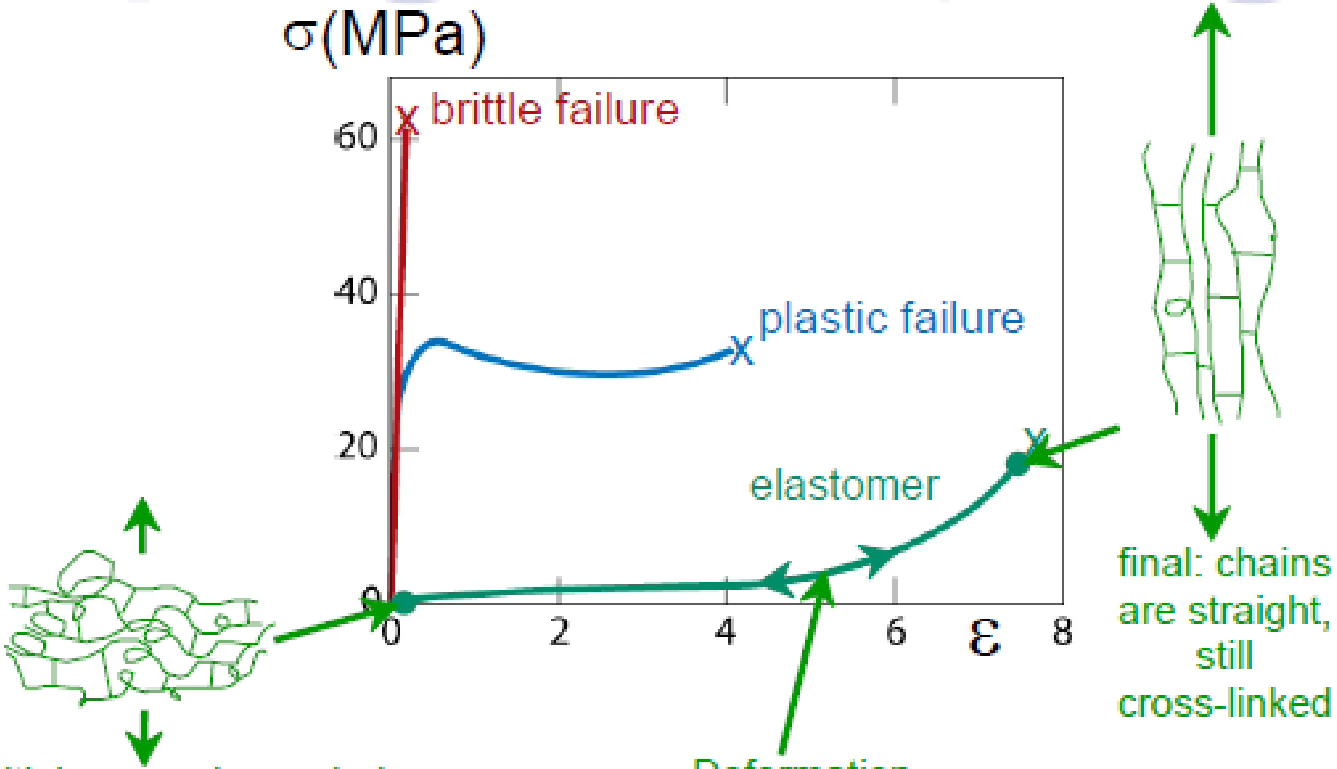
Lamella crystalline region

Initial stage- elongation of amorphous tie chain

crystalline regions align

crystalline region aligned due to starching of crystalline regions

Tensile Response: Elastomer Case



initial: amorphous chains are kinked, cross-linked.

Deformation is reversible!

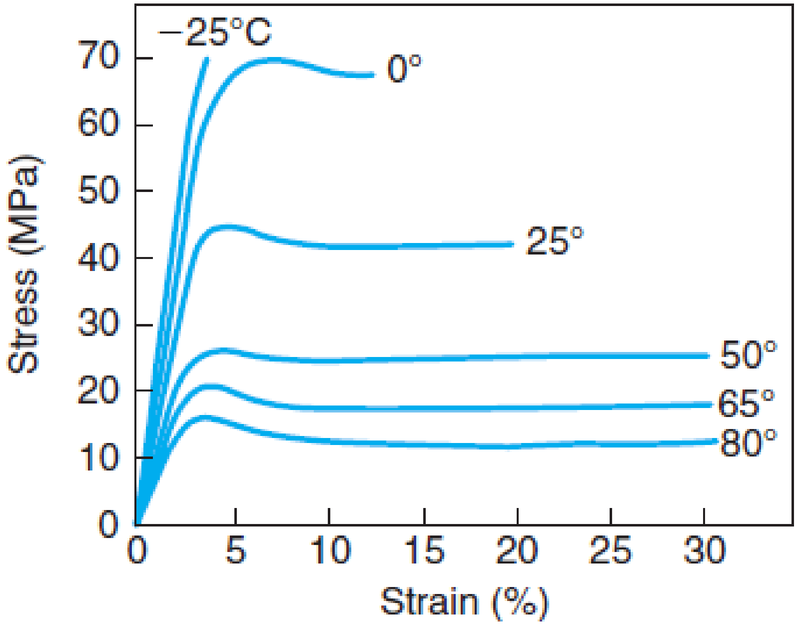
final: chains are straight, still cross-linked

Thermal and Electrical Properties

- Plastics has low thermal and electrical conductivity, low specific gravity, high coefficient of thermal expansion and low electrical conductivity
- Electrical conductivity can be increased by **doping**
- Electrical conductivity of polymers increases with moisture absorption

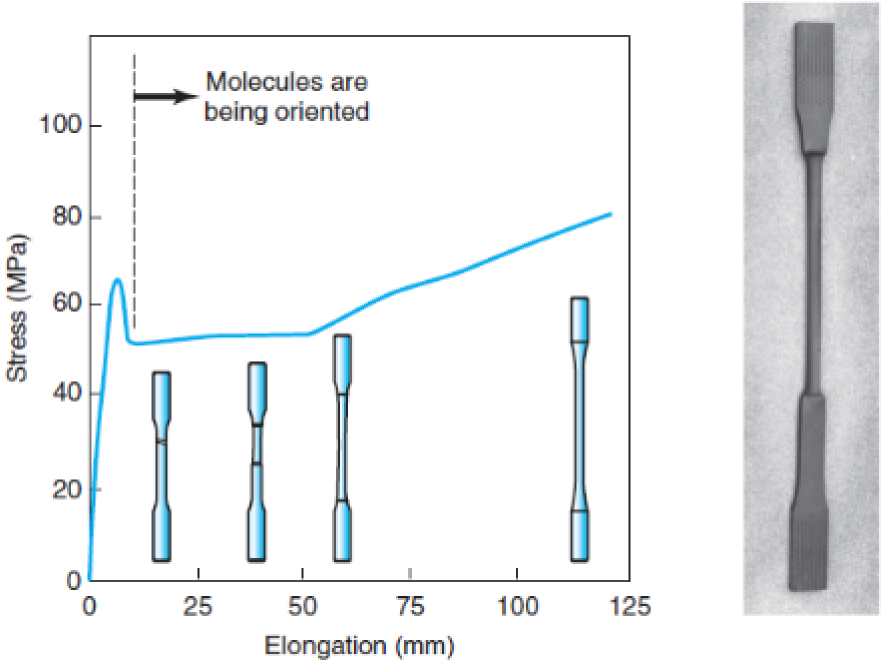
Effects of Temperature

- When above T_g thermoplastic polymer becomes *leathery* and *rubbery*
- At higher temperatures it becomes a *viscous fluid*
- Viscosity also decreases with increasing temperature



Effect of Rate of Deformation

- When deformed rapidly, behavior of thermoplastics is similar to metals
- Thermoplastics can undergo large *uniform deformation* in tension before fracture



(a)

(b)

Effect of Water Absorption

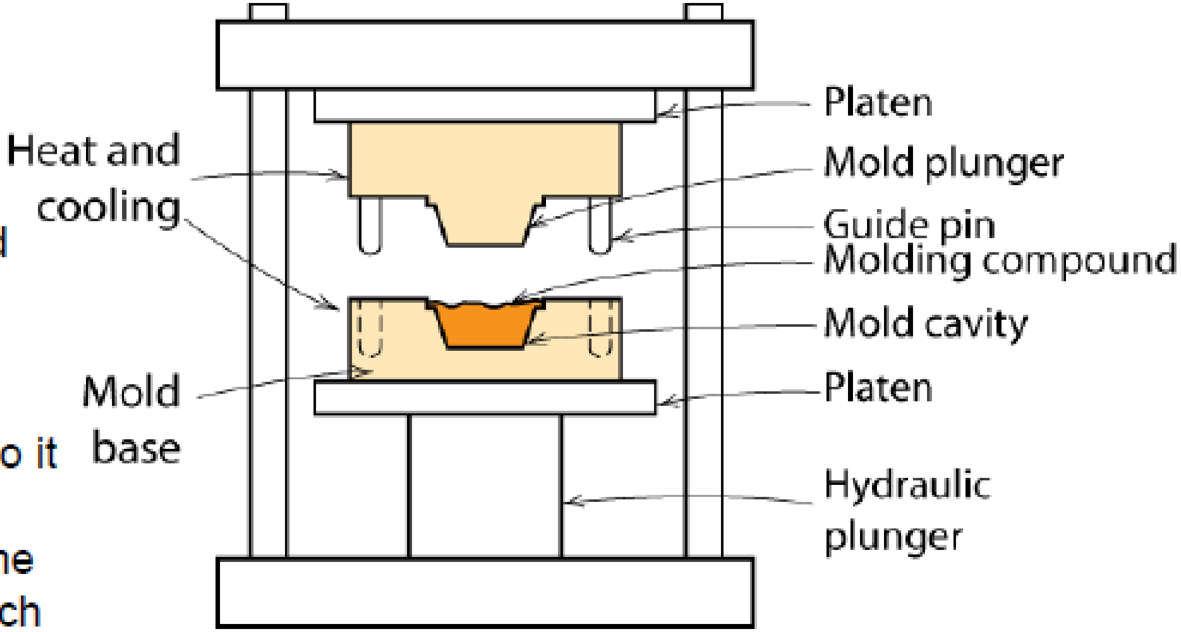
- Some polymers has ability to absorb water (*hygroscopic*)
- Water acts as a plasticizing agent and makes the polymer more plastic
- With increasing moisture absorption, the T_g, yield stress, and elastic modulus of the polymer are lowered

Additives in Plastics

- To impart certain specific properties, polymers are compounded with *additives*
- **Plasticizers** are added to polymers to impart *flexibility* and *softness*
- *Ultraviolet radiation* and *oxygen* cause polymers to degrades and becomes stiff and brittle
- **Fillers** improve strength, hardness, toughness, abrasion resistance, dimensional stability
- **Lubricants** added to reduce friction

Processing Plastics - Molding

- **Compression and transfer molding**
  - **thermoplastic or thermoset**



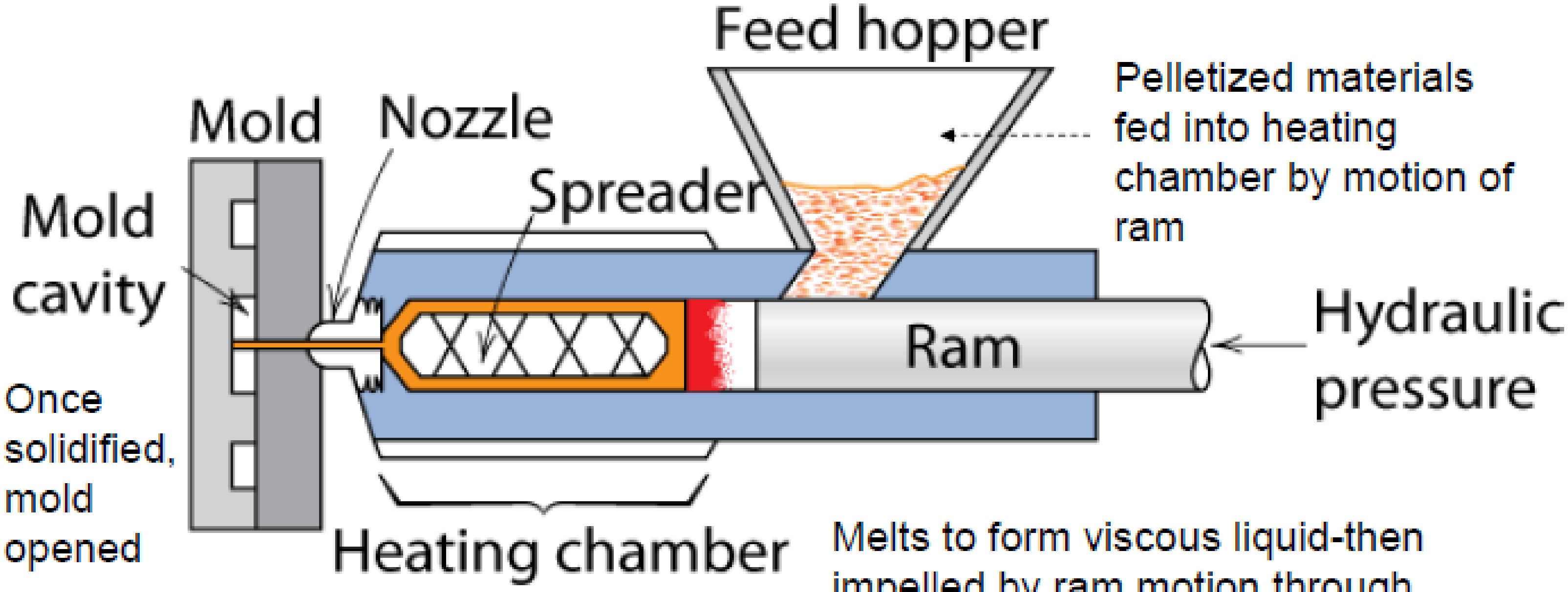
Mixed polymer and additives placed in mold cavity

Both mold are heated

One mold is movable, so it is closed and heat and pressure applied-become viscous and flow to match to the mold shape

Processing Plastics - Molding

- **Injection molding**
  - ○ **thermoplastic & some thermosets**

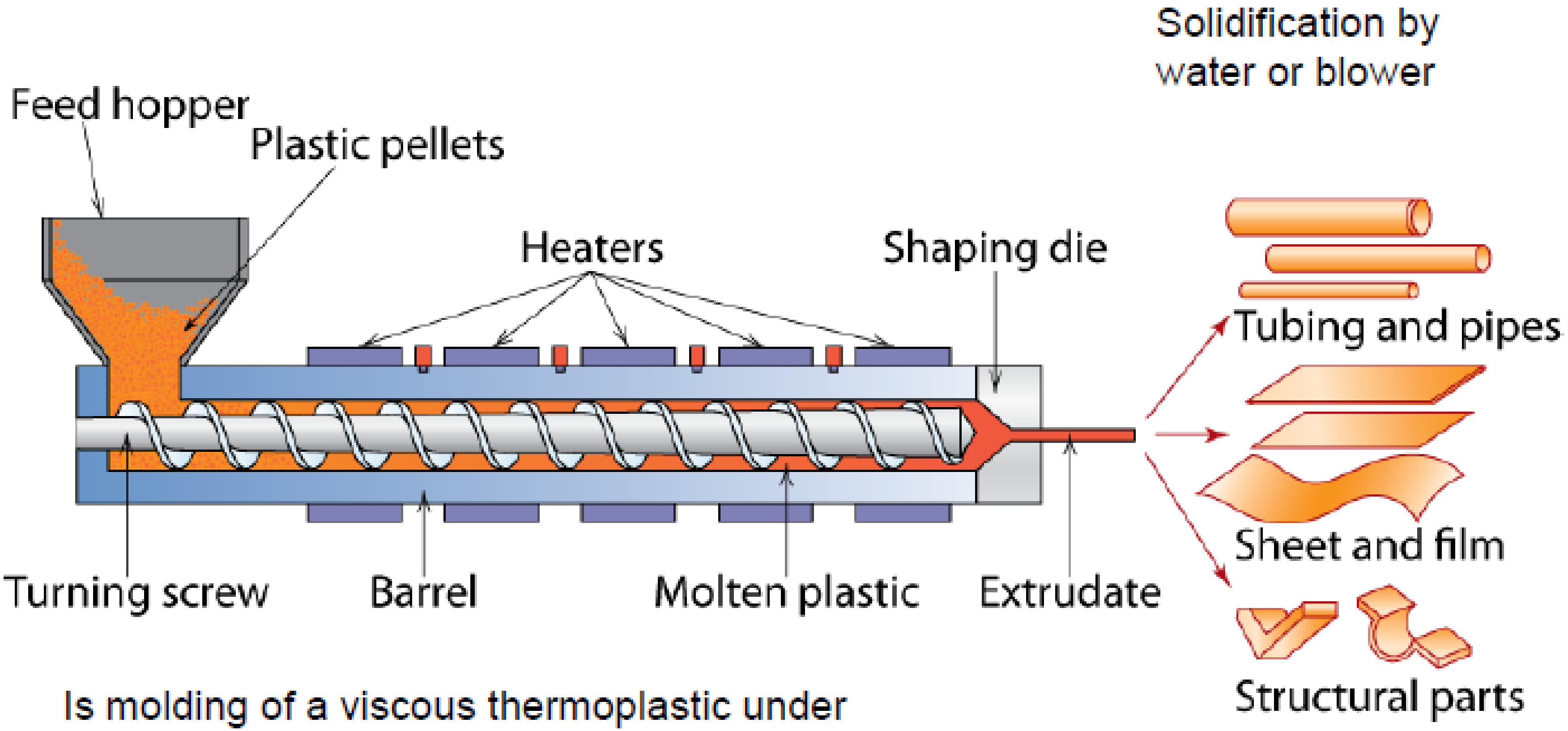


Pelletized materials fed into heating chamber by motion of ram

Once solidified, mold opened

Melts to form viscous liquid-then impelled by ram motion through nozzle to cavity

Processing Plastics – Extrusion



Is molding of a viscous thermoplastic under pressure through an open ended die

Fabrication of Fibre

Materials is heated→viscous liquid → pumped through spinneret (small holes) → fibre formed → solidified by cooling

Two technique

1. Dry spinning

Polymer dissolved in volatile solvent → pump through spinneret into heated zone → fibre solidify as solvent evaporate

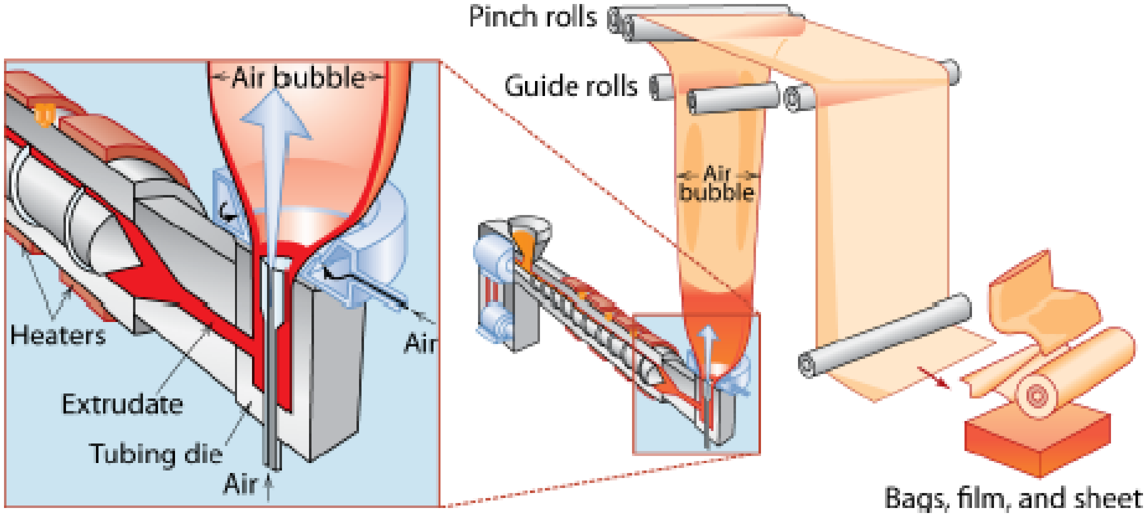
2. Wet spinning

Fibre formed by passing a polymer solvent solution through spinneret direct into second solution that form fibres (precipitation)

Fabrication of film

Film are extruded through die slit, followed by rolling or drawing to reduce thickness and improve strength

Or film can be blown-continuous tubing is extruded through die, then by applying gas pressure inside the tube and by drawing the film in axial direction the materials expands around trapped air bubble-the wall thickness reduces and form cylindrical film which can be sealed at end to make bags



Advanced Polymers

- **Ultrahigh molecular weight polyethylene (UHMWPE)**
  - **Molecular weight ca. 4×10^6 g/mol**
  - **Excellent properties for variety of applications**
    - **bullet-proof vest, golf ball covers, hip joints, etc.**

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