# ENGG103 – Materials in Design

## Week 6: Polymers

UNIVERSITY
OF WOLLONGONG
IN DUBAI


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Consultation hours:

Tuesday 09:30-11:30

https://uow.webex.com/meet/ciara

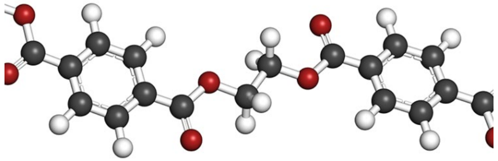
Please email first for appointment.

# Chapter 14: Polymer Structures

## ISSUES TO ADDRESS...

- What are the general structural and chemical characteristics of polymer molecules?
- What are some of the common polymeric materials, and how do they differ chemically?
- How is the crystalline state in polymers different from that in metals and ceramics ?

# Origin of Polymers



Polymers
(long chain molecules)

Natural Polymers
(Proteins etc. obtained from plants, animals or bacteria)

Synthetic Polymers
(Industrially produced from oil)

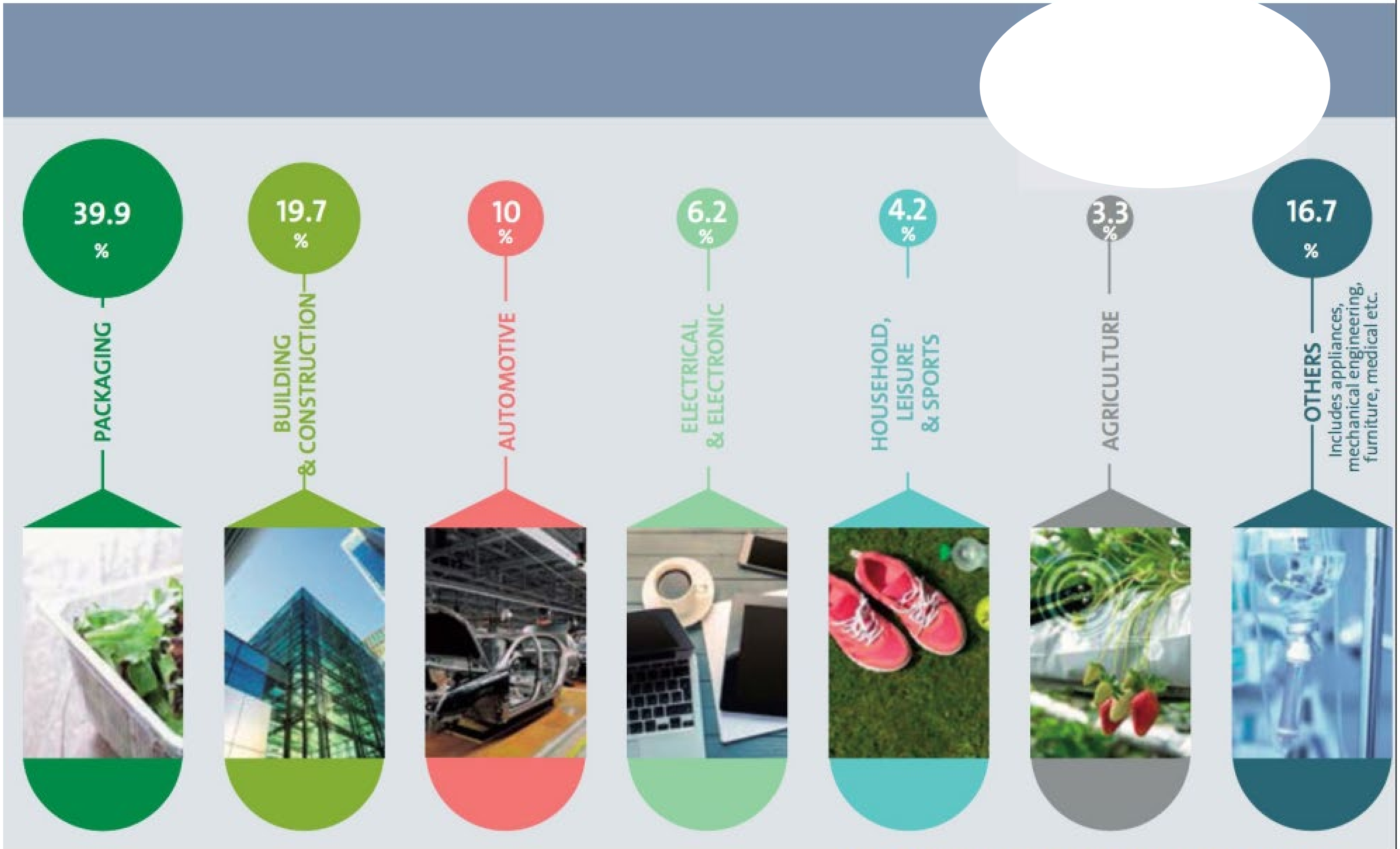
Cotton
Wool
Silk
Cellulose
Latex rubber

Textile Fibres
Paper
Natural Rubber
Food additives
Biodegradable Plastics
Biomaterials

Polyethylene
Polypropylene
Polystyrene
PVC, PET, PUR

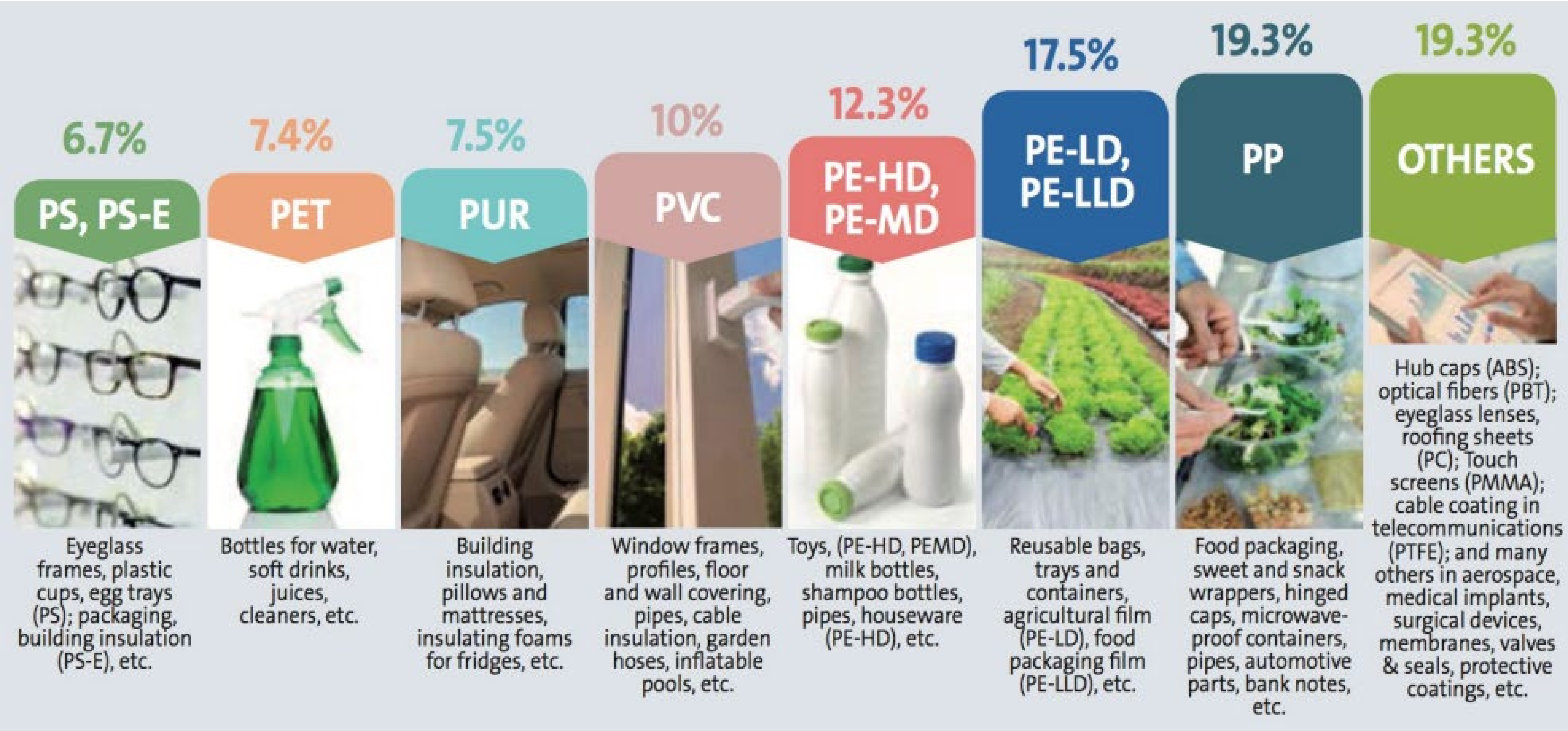
Textile Fibres
Film
Synthetic Rubber
Extrusions and Mouldings

# Where are polymers used?




https://journals.openedition.org/factsreports/5071

# What are the major polymers used?

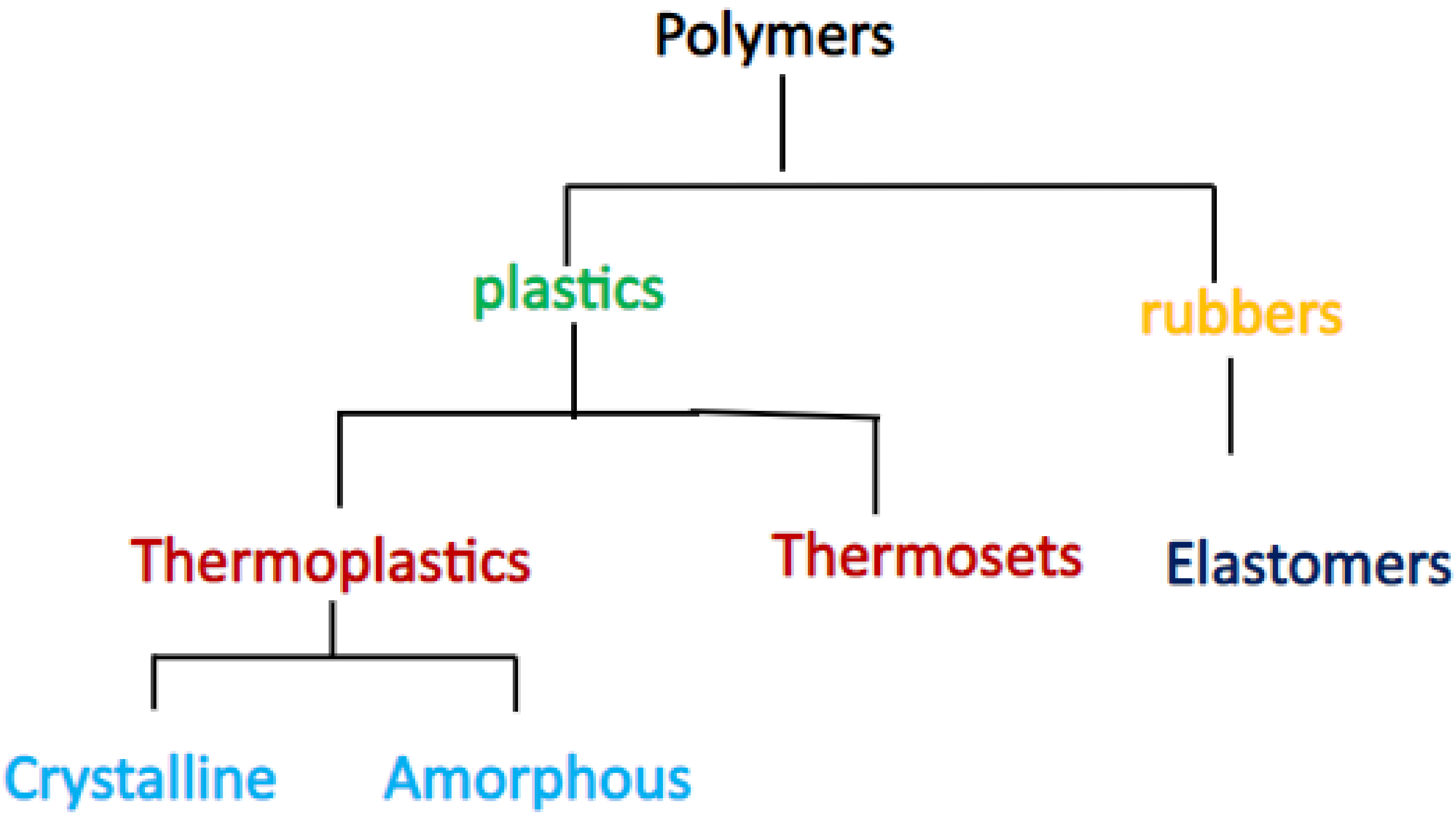



**PE, PP, PVC, PUR, PET and PS account for 80% of the world consumption of polymers**

https://journals.openedition.org/factsreports/5071

# Polymer Classification

Polymers are commonly classified according to thermal effect as follows:




**Thermoplastics**: soften when heated, become hard and rigid again when cooled
**Thermosetting:** do not become soft on heating

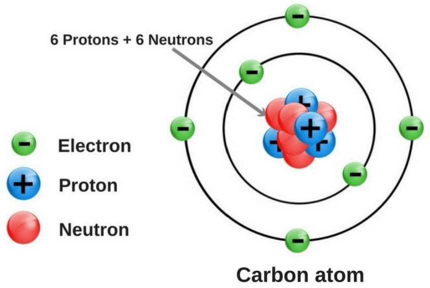
# What is a Polymer?

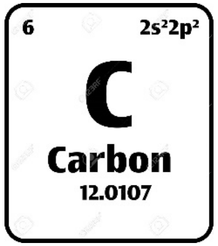
Poly mer

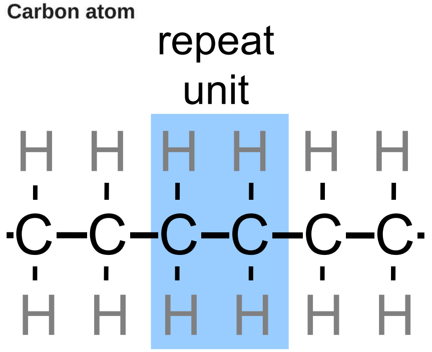
many repeat unit

H — Hydrogen

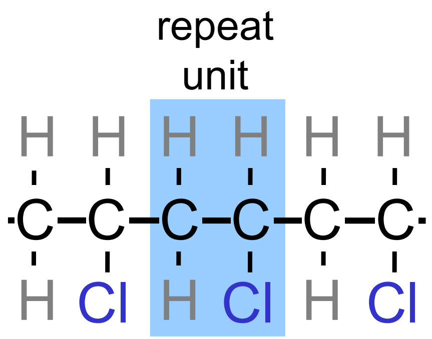
C — Carbon



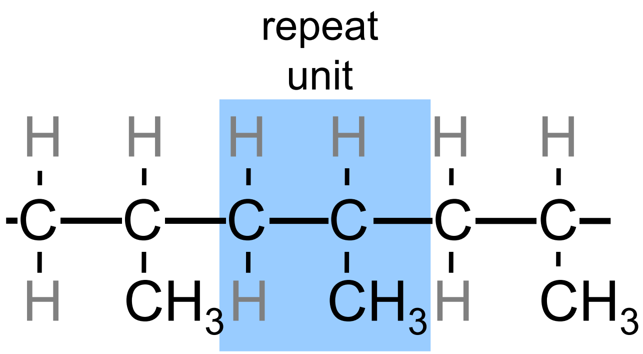




Polyethylene (PE)

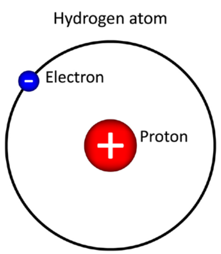


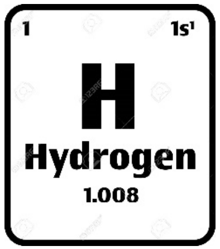

Poly(vinyl chloride) (PVC)

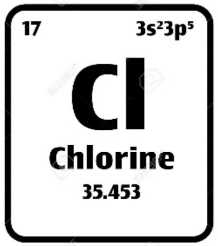



Polypropylene (PP)

Adapted from Fig. 14.2, *Callister & Rethwisch 8e.*

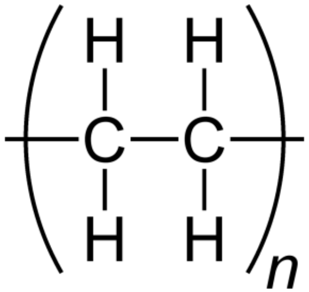


# Introduction - Polymers **Poly (many)** + **mer (unit)**

- Material composed by long molecular chains, that is built from smaller units (monomer)
- Polymers consist of several ordered **monomer** repeat units
- Polymer structure connected by covalent bonds (Sharing of e's)

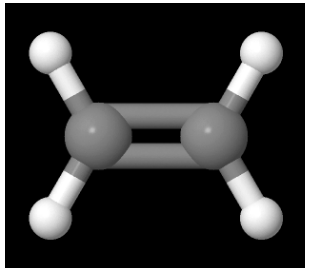


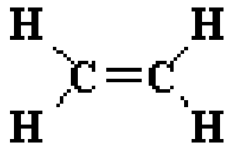
PE – Poly(ethylene)

Polyethylene is the commonest of the thermoplastics

**Ethylene**

Each carbon atom has 4 electrons that may be covalently bonded, the hydrogen atom has 1 electron for bonding





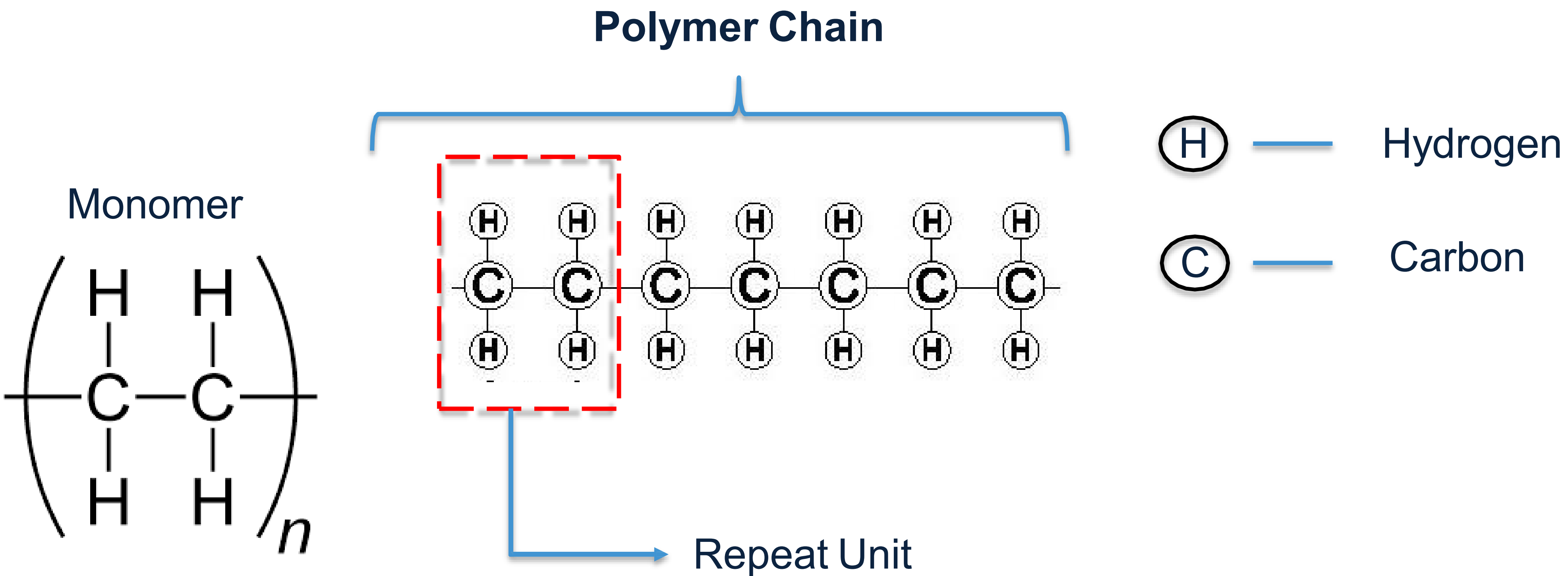
Source

- This is the polymer that makes grocery bags, shampoo bottles, children's toys, and even bullet proof vests.
- For such a versatile material, it has a very simple structure, the simplest of all commercial polymers.

# Thermoplastics

## PE – Poly(ethylene)

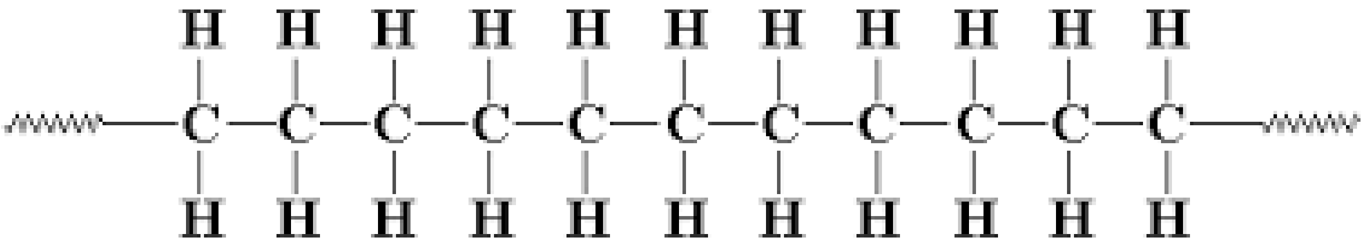
- They are often described as **linear polymers**, that is the chains are not cross-linked
- That is why they soften if the polymer is heated: the secondary bonds which bind the molecules to each other melt so that it flows like a viscous liquid, allowing it to be formed.



# Thermoplastics

## PE – Poly(ethylene)

- The chemical reaction forming polymers from monomers is called **polymerization**
- In the end of polymerization, long chains are obtained



# Polymers

- The molecules in linear polymers have a **range of molecular weights**, and they **pack together** in a **variety of configurations**.
- Some, like polystyrene, are amorphous; others, like polyethylene, are partly crystalline.

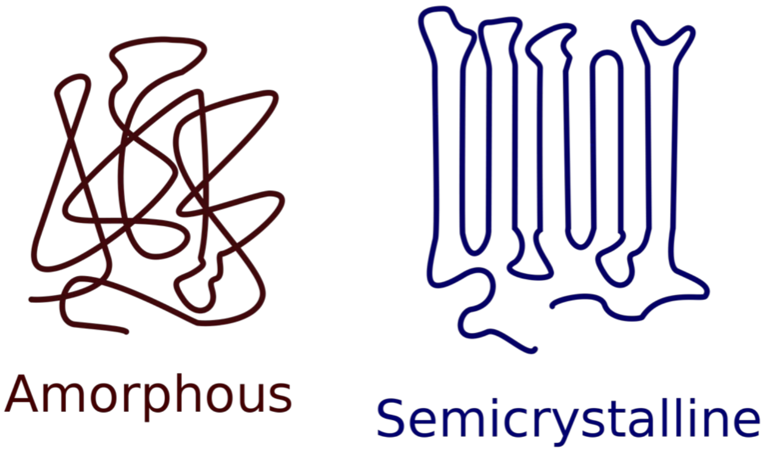


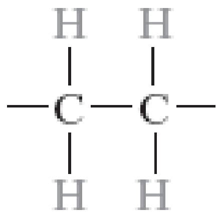
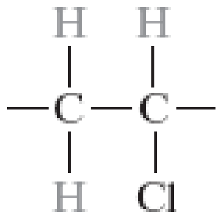
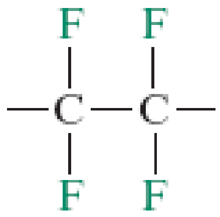
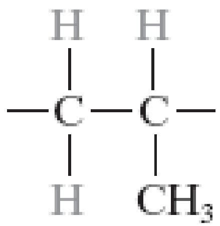

Image via Quora

- This range of molecular weights and packing geometries means that **thermoplastics do not have a sharp melting point**.
- Instead, their viscosity falls over a range of temperature, like that of an inorganic glass.


Chemistry
THERMOSETTING &
THERMOSOFTENING

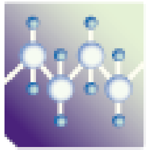
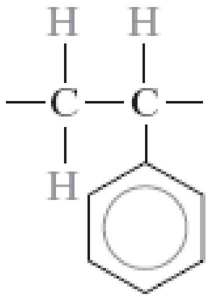
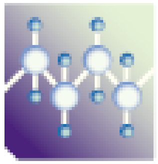
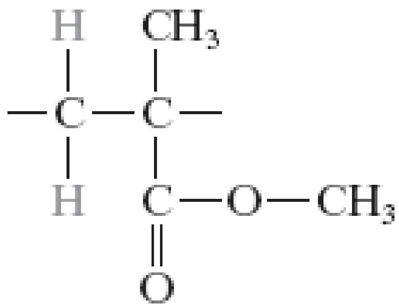
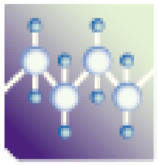
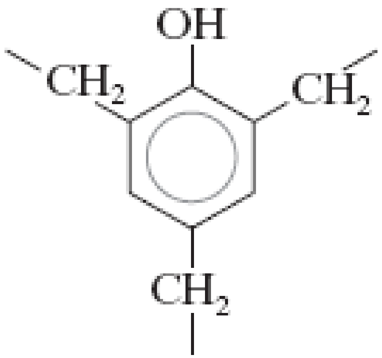
# Bulk or Commodity Polymers

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

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

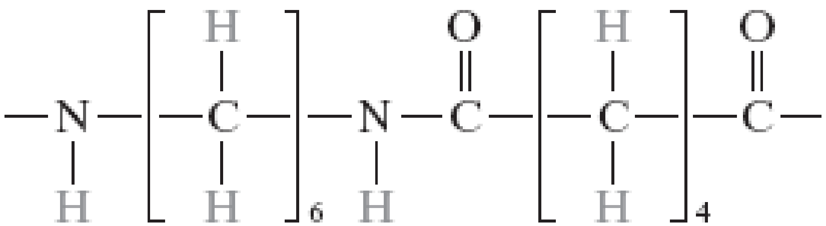
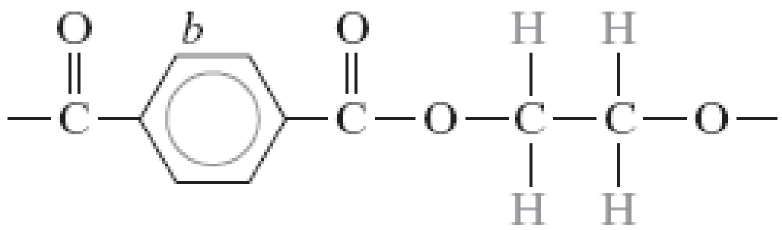
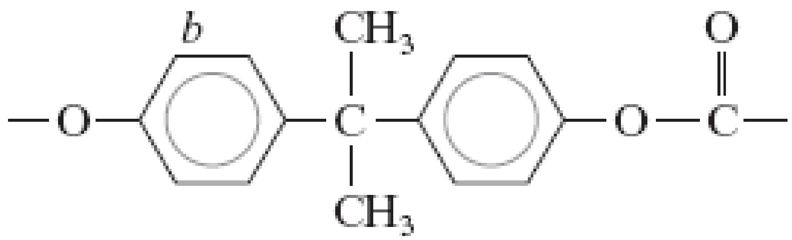
# Bulk or Commodity Polymers (cont)

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

| *Polymer* | *Repeat Unit* |
|---|---|
|  Polystyrene (PS) |  |
|  Poly(methyl methacrylate) (PMMA) |  |
|  Phenol-formaldehyde (Bakelite) |  |

# Bulk or Commodity Polymers (cont)

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

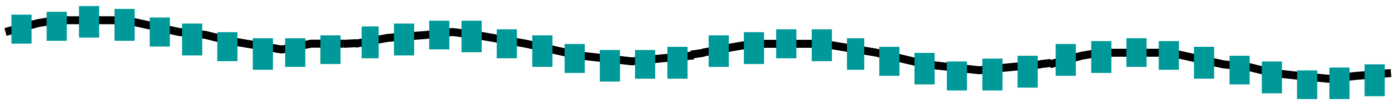
| *Polymer* | *Repeat Unit* |
|---|---|
| Poly(hexamethylene adipamide) (nylon 6,6) |  |
| Poly(ethylene terephthalate) (PET, a polyester) |  |
| Polycarbonate (PC) |  |

# MOLECULAR WEIGHT

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

Low *M*

The molecular weight of a polymer is directly related to its properties. As the molecular weight increases, mechanical properties generally increase.



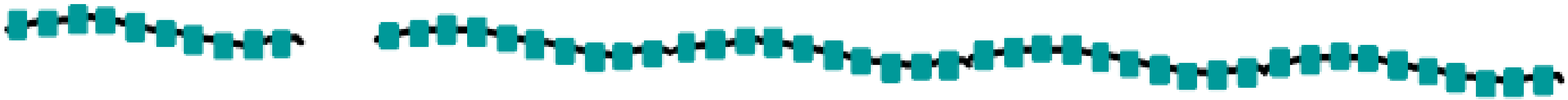
high *M*

Every polymer has an ideal molecular weight at which the balance of different properties (such as processability, strength, brittleness etc.) is optimized.

Not all chains in a polymer are of the same length
— i.e., there is a distribution of molecular weights

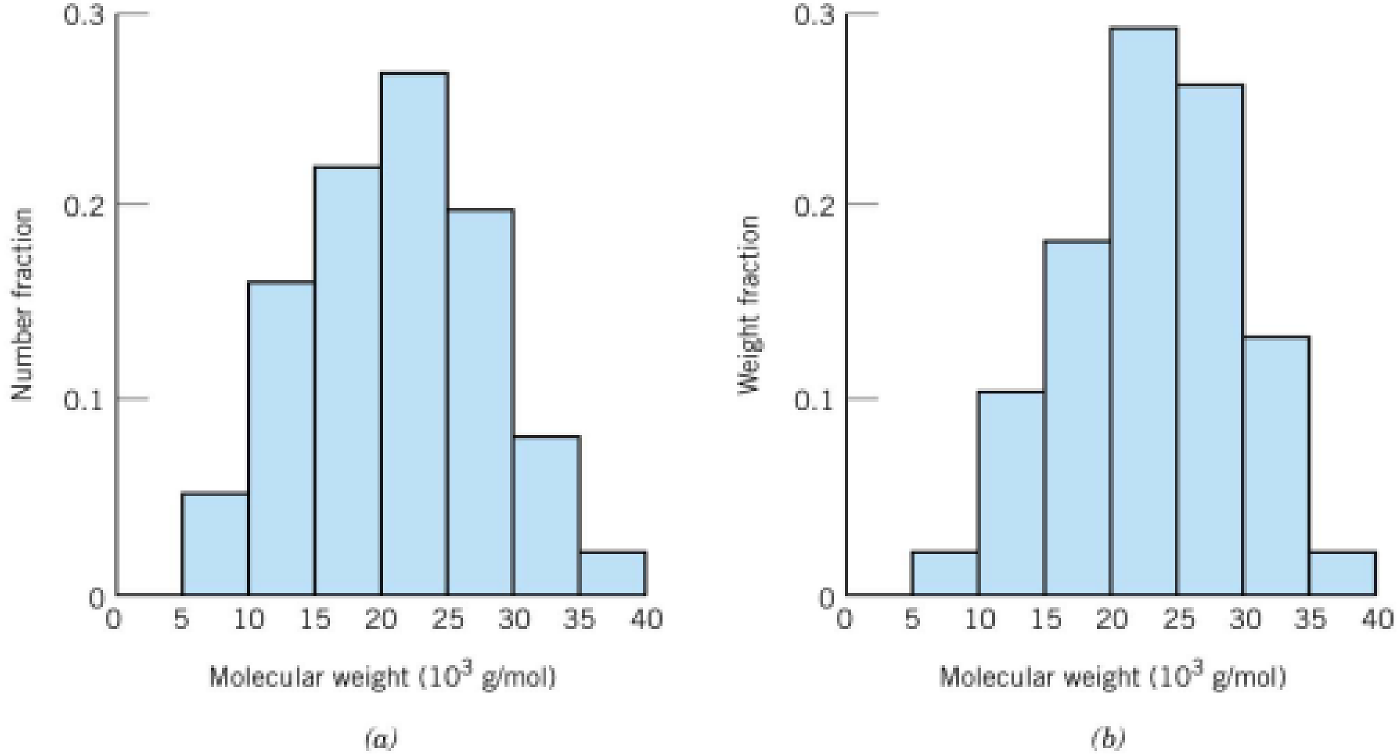
# MOLECULAR WEIGHT & SIZE

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

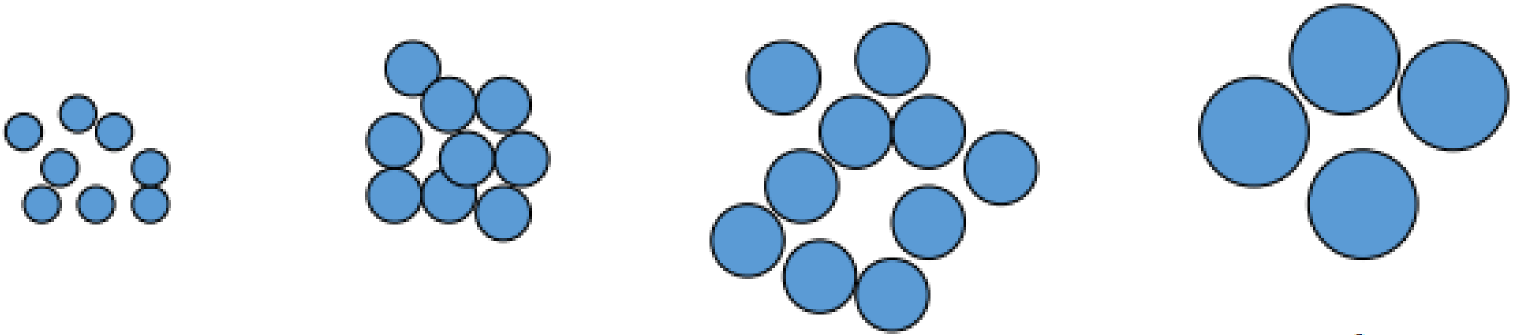


**smaller $M_W$** **larger $M_W$**

**FIGURE 14.3** Hypothetical polymer molecule size distributions on the basis of (*a*) number and (*b*) weight fractions of molecules.



# MOLECULAR WEIGHT AVERAGES



$n_1 = 8$ $M_1 = 1000$ g/mol

$n_2 = 9$ $M_2 = 10000$ g/mol

$n_3 = 10$ $M_3 = 100000$ g/mol

$n_4 = 4$ $M_4 = 1000000$ g/mol

**Number Average Molecular Weight**

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i} \qquad \overline{M}_n = \frac{(8\times 1000 + 9\times 10000 + 10\times 100000 + 4\times 1000000)}{(8+9+10+4)}$$

$$\overline{M}_n = 164{,}450 \text{ g/mol}$$

*Callister (Eqn. 14.5a) uses this formula:*

$$\overline{M}_n = \sum x_i M_i = \frac{1}{\sum n_i}\sum n_i M_i$$

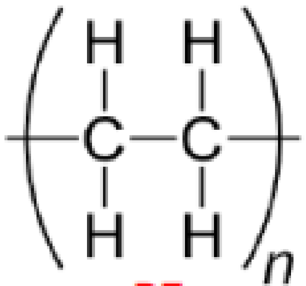
*Where $x_i$ is the number fraction of molecules in each group*

**Weight Average Molecular Weight**

$$\overline{M}_w = \frac{\sum W_i M_i}{\sum W_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i} \qquad \overline{M}_w = 804{,}415 \text{ g/mol}$$

# Size of Polymer Molecules

## Extended Chain Length – length of a fully stretched out linear chain

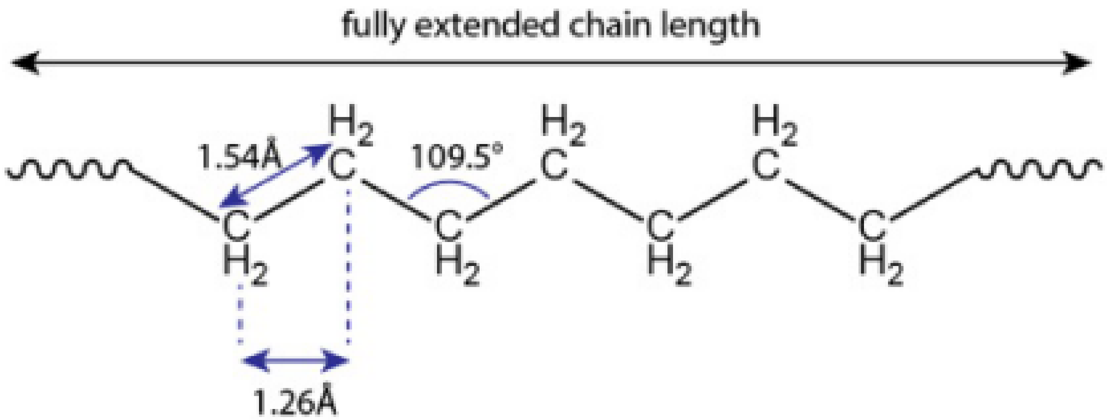



PE

**Example: Calculate the Extended Chain Length of Polyethylene with n = 10,000**

C-C single bond length = 0.154 nm but C-C single bonds are arranged in a zig-zag shape with a bond angle of ø=109.5°

$0.154 \times \sin(ø/2) = 0.126$ nm

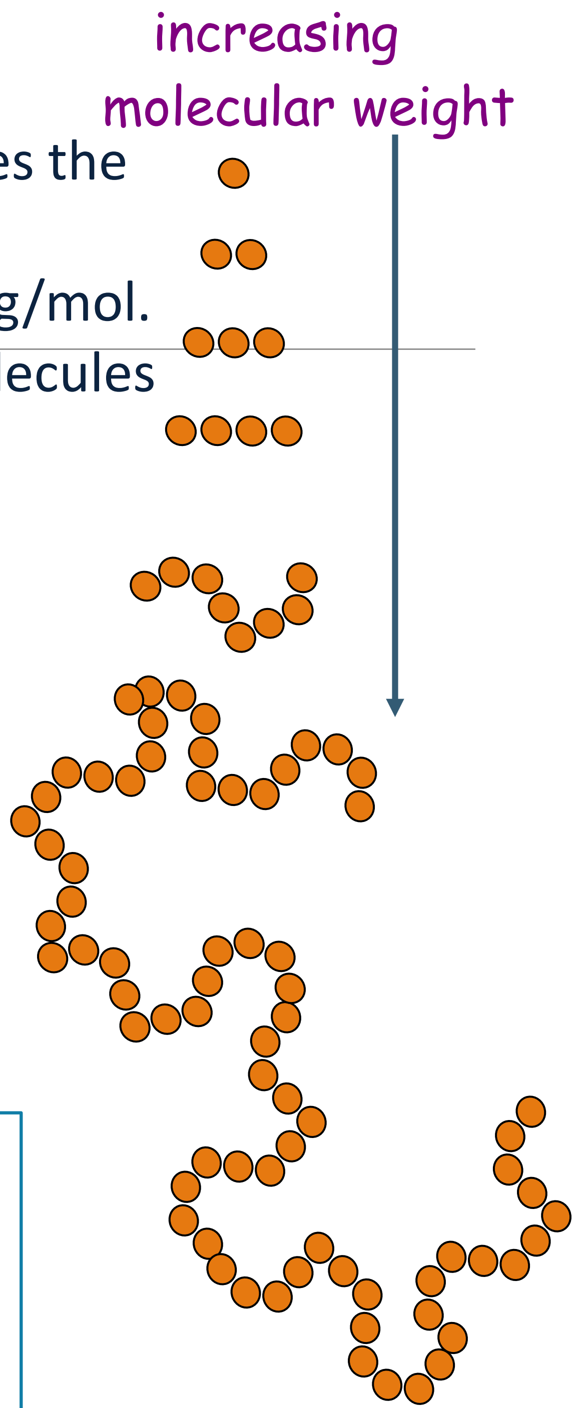



There are 2 C-C single bonds per repeat unit in PE:

Extended Chain Length = $2 \times 0.126 \times 10{,}000 = 2{,}520$ nm (2.52 μm)

# Degree of polymerization (DP)

- The molecular weight of a polymer is simply the DP times the molecular weight of the monomer.
- Ethylene, $C_2H_4$, for example, has a molecular mass of 28 g/mol.
- If the DP for a batch of polyethylene is $10^4$, then the molecules have an average molecular weight ($\bar{M}_n$) of 280,000.

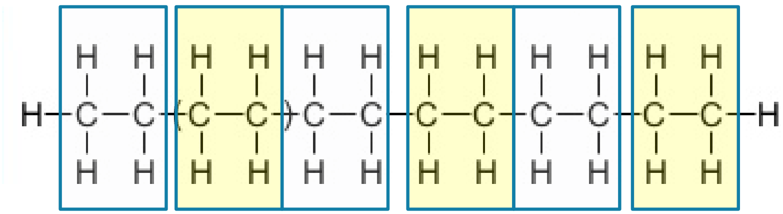



Degree of polymerization (DP)

$$\boxed{DP = \frac{\bar{M}_n}{m}}$$

where

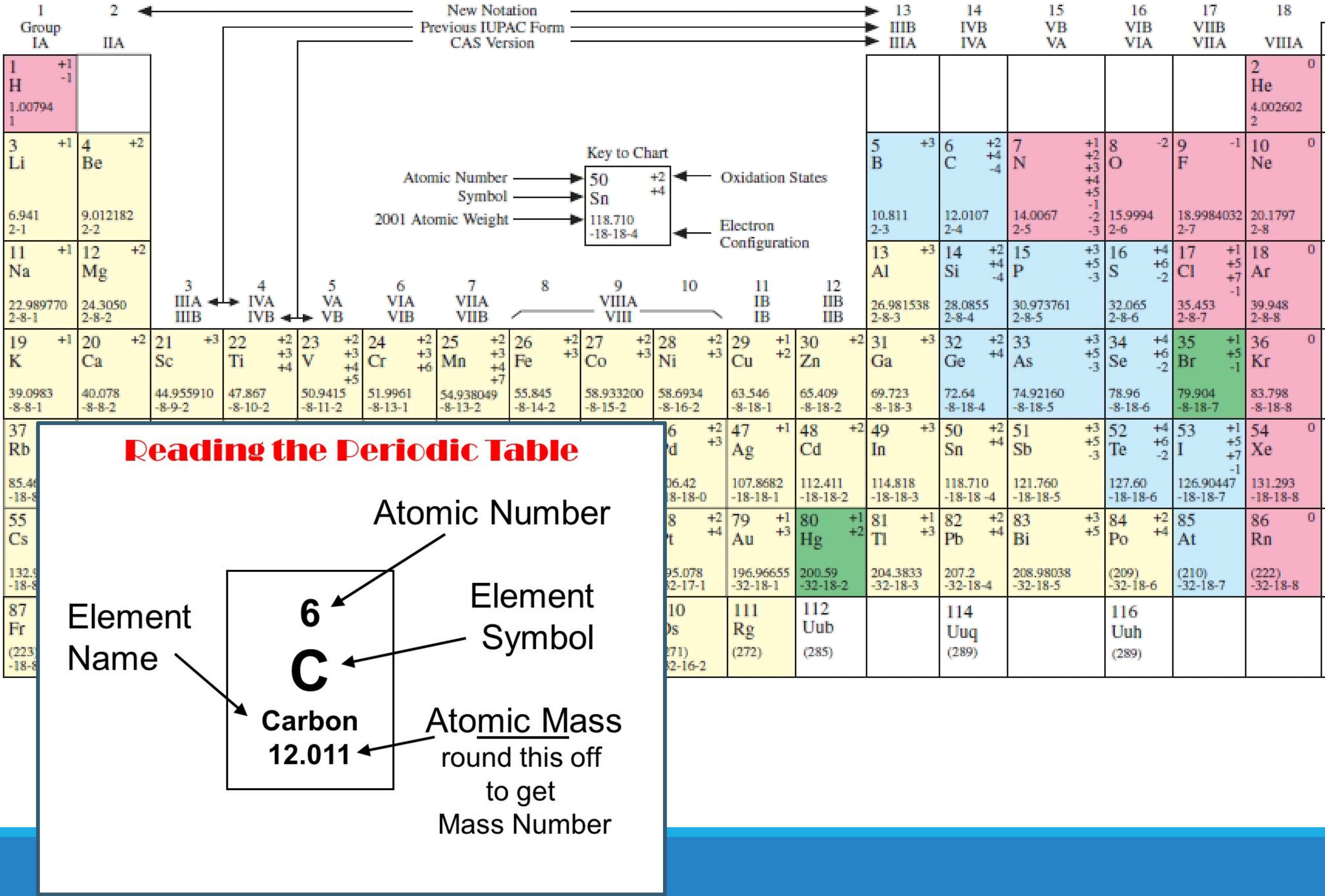
- $\bar{M}_n$ is the molecular weight of the polymer chain
- $m$ is the molecular weight of the monomer (repeat unit)



$n_i = 6$

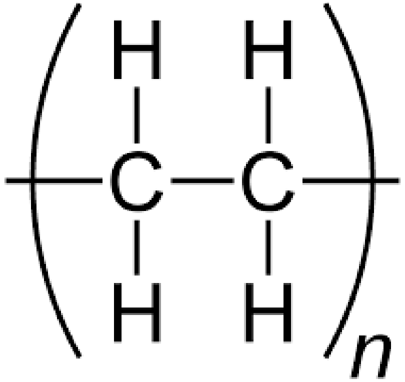
n= number of repeat units per chain

# Periodic Table



# Example 8.3

If we think about **PE** molar mass ($m_a$):

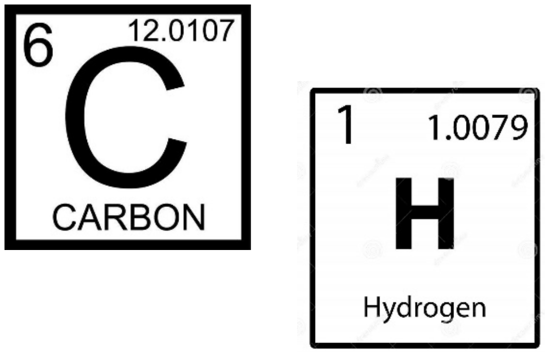



$$m = (2x12) + (4x1) = 28\frac{g}{mol}$$

- If **(n) DP**= 10,000

How much does a *mole* of PE weight?

$$DP = \frac{\bar{M}_n}{\bar{m}} \qquad 10{,}000 = \frac{\bar{M}_n}{28}$$



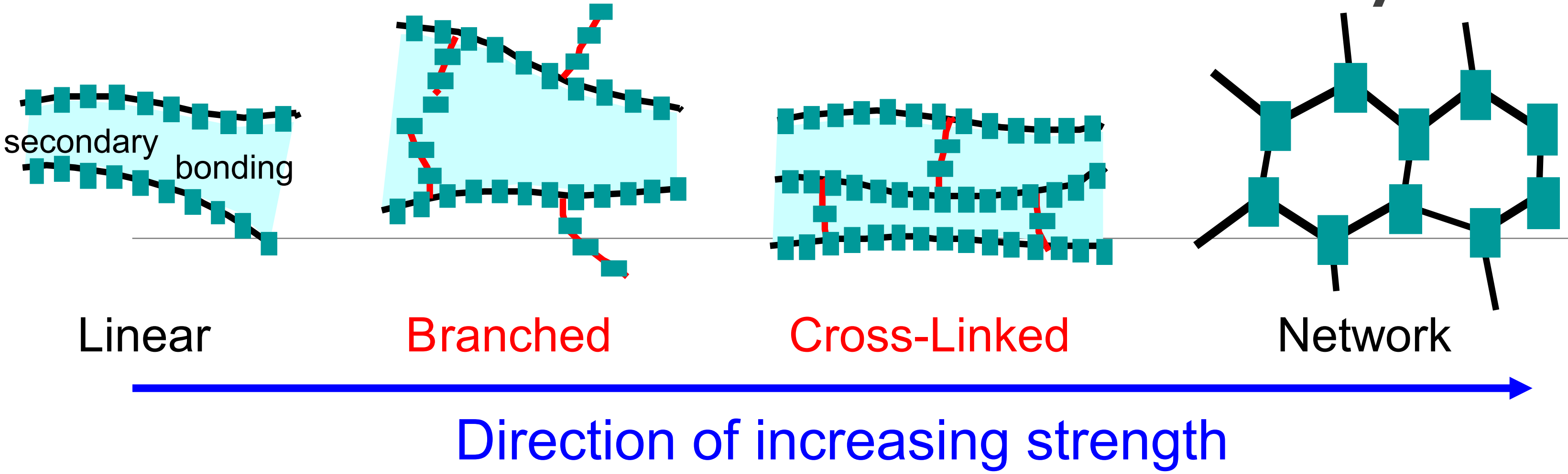

$M_n$ = 280,000 g/mol or Da (Dalton)

H — 1.008 g/mol

C — 12.01 g/mol

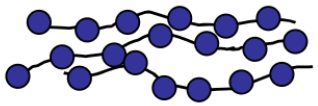
This for a single PE chain

# Molecular Structures for Polymers

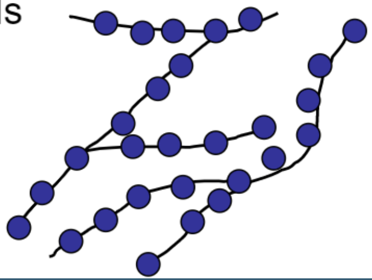



Adapted from Fig. 14.7, *Callister & Rethwisch 8e.*

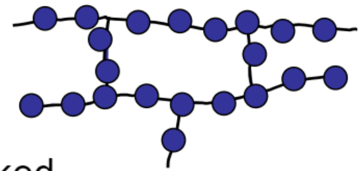
- Linear
  - Tangled covalently bonded chains
  - Secondary interchain bonds



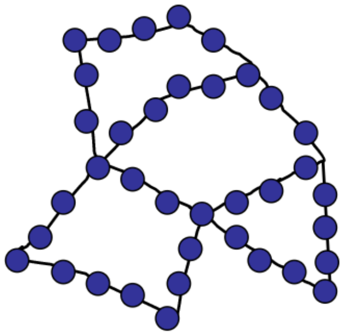
- Branched
  - Tangled covalently bonded chains with side branches
  - Secondary interchain bonds



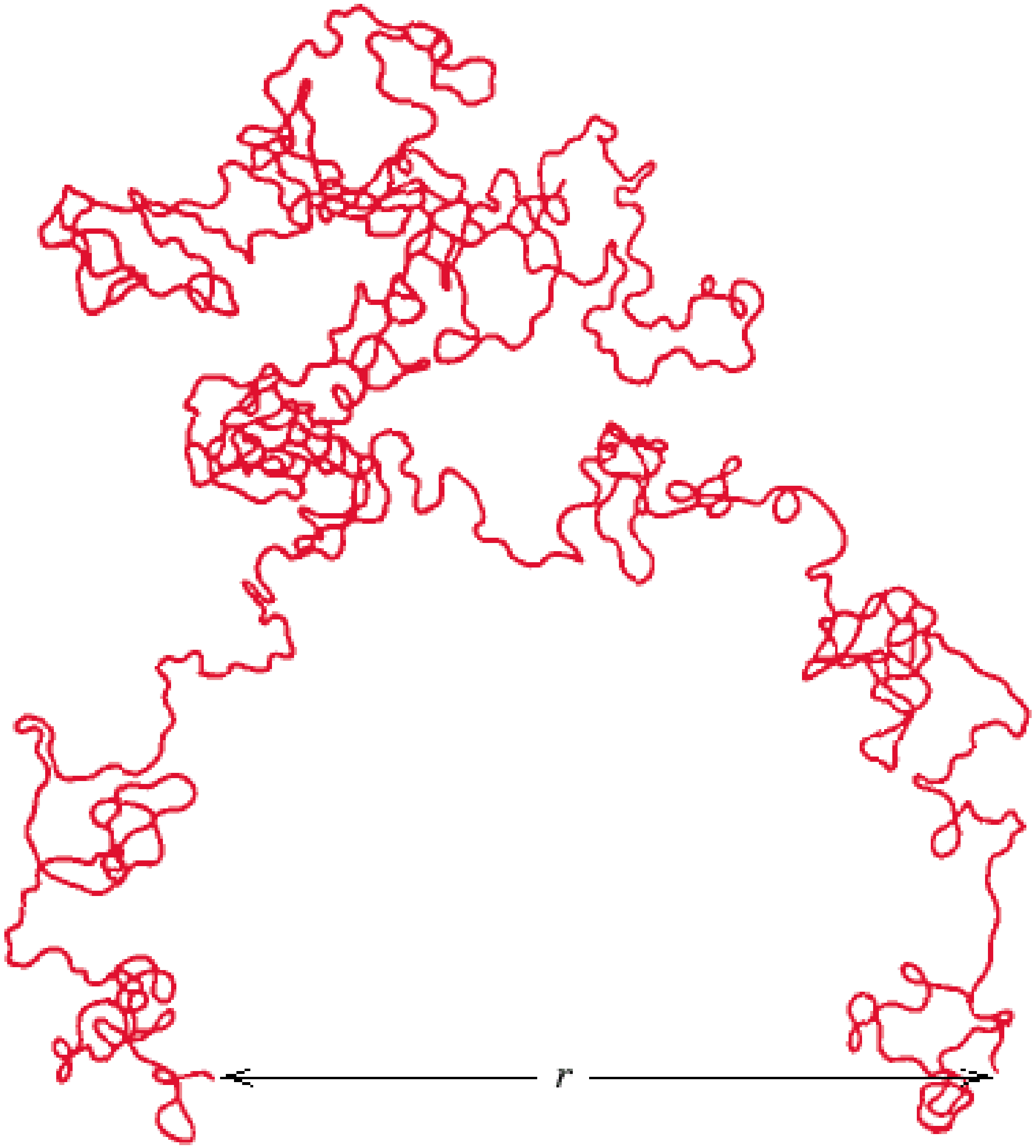
- Crosslinked
  - Tangled covalently bonded chains
  - Covalent and secondary interchain bonds



- Networked
  - Highly crosslinked polymer



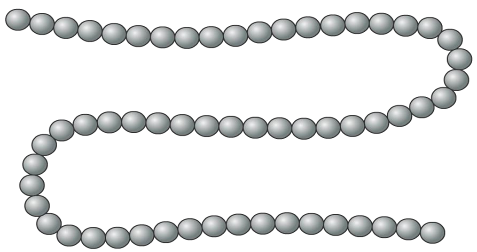
# Chain End-to-End Distance, *r*




Adapted from Fig. 14.6, *Callister & Rethwisch 8e.*

# Total chain length

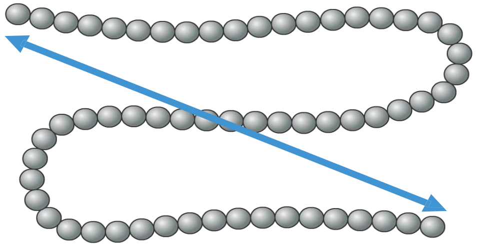
- For a linear polymer molecule, the total chain length **L** depends on the bond length between chain atoms ***d***, the total number of bonds in the molecule **n**, and the angle between adjacent backbone chain atoms **θ**



$$\boxed{L = nd.\sin(\frac{\theta}{2})}$$

- The average end-to-end distance for a series of polymer molecules r is equal to

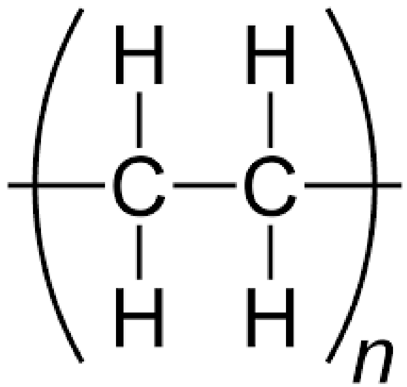
$$\boxed{r = d\sqrt{n}}$$

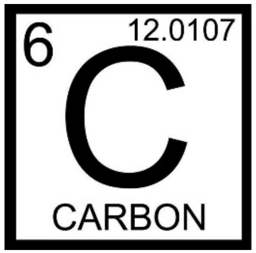


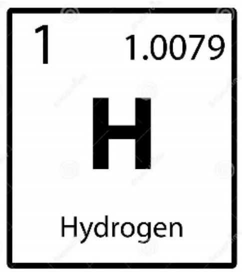
***r*** - chain end – to – end distance
***d*** – distance between the C – C
n – number of C – C bonds in the molecule

# Example 8.4

a) Calculate the average of **total chain length**, L, for a linear polyethylene polymer with a average molecular weight ($\bar{M}_n$) of 300,000 g/mol?






H — 1.008 g/mol

C — 12.01 g/mol

$$n = \boxed{DP = \frac{\bar{M}_n}{m_a}}$$

$$\boxed{L = nd.\sin(\frac{\theta}{2})}$$

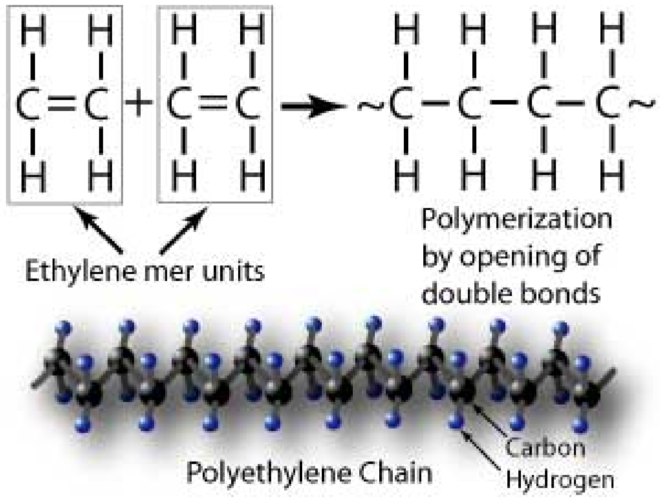
$m_{a(PE)}$ = 12*2(C)+1*4(H) = 28 g/mol

$$DP = \frac{M_n}{m} = \frac{300{,}000}{28} = \mathbf{10{,}714 = n}$$

The number of repeating units along the chain

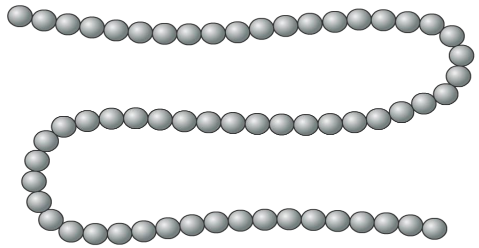
# Example contd.

Two C – C in each monomer, there will be a total of (2*10,714 = 21,428) chain bonds in the molecule n.




Given in question C – C = 0.154 nm, θ= 109º for PE

$$\boxed{L = nd.\sin(\frac{\theta}{2})}$$



$$L = 10{,}714 * 2 * 0.154.\sin(\frac{109}{2})$$

$$\boxed{L = 2686\ nm}$$

b) The average end-to-end distance for a series of polymer molecules r is equal to

$$\boxed{r = d\sqrt{n}}$$

$$r = 0.154(nm)\sqrt{21{,}428} = 22.5\ nm$$

# Spatial Arrangement

Spatial arrangement of atoms concern how different atomic particles and molecules are situated about in the space around the organic compound, namely its carbon chain.

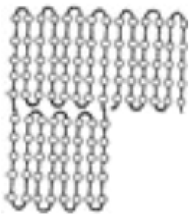
In this sense, spatial arrangement of a molecule are different to one another if an atom is shifted in any three-dimensional direction by even one degree. This opens up a very broad possibility of different molecules, each with their unique placement of atoms in three-dimensional space.

**Stereoisomerism** is the arrangement of atoms in molecules whose connectivity remains the same but their arrangement in space is different in each isomer.

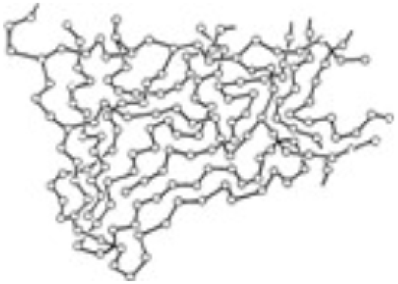
Different spatial organization of the monomers controls the strength, glass transition temperature, melting point, solubility etc.

# Polymer Classifications II

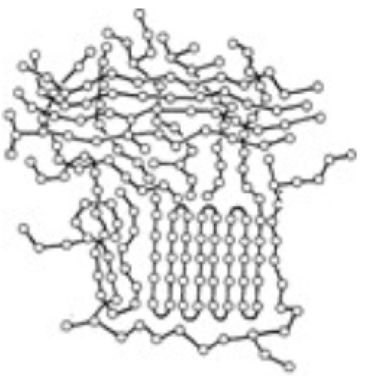
- ***Crystalline*** :
  - Periodic 3-D, repeating array of molecules

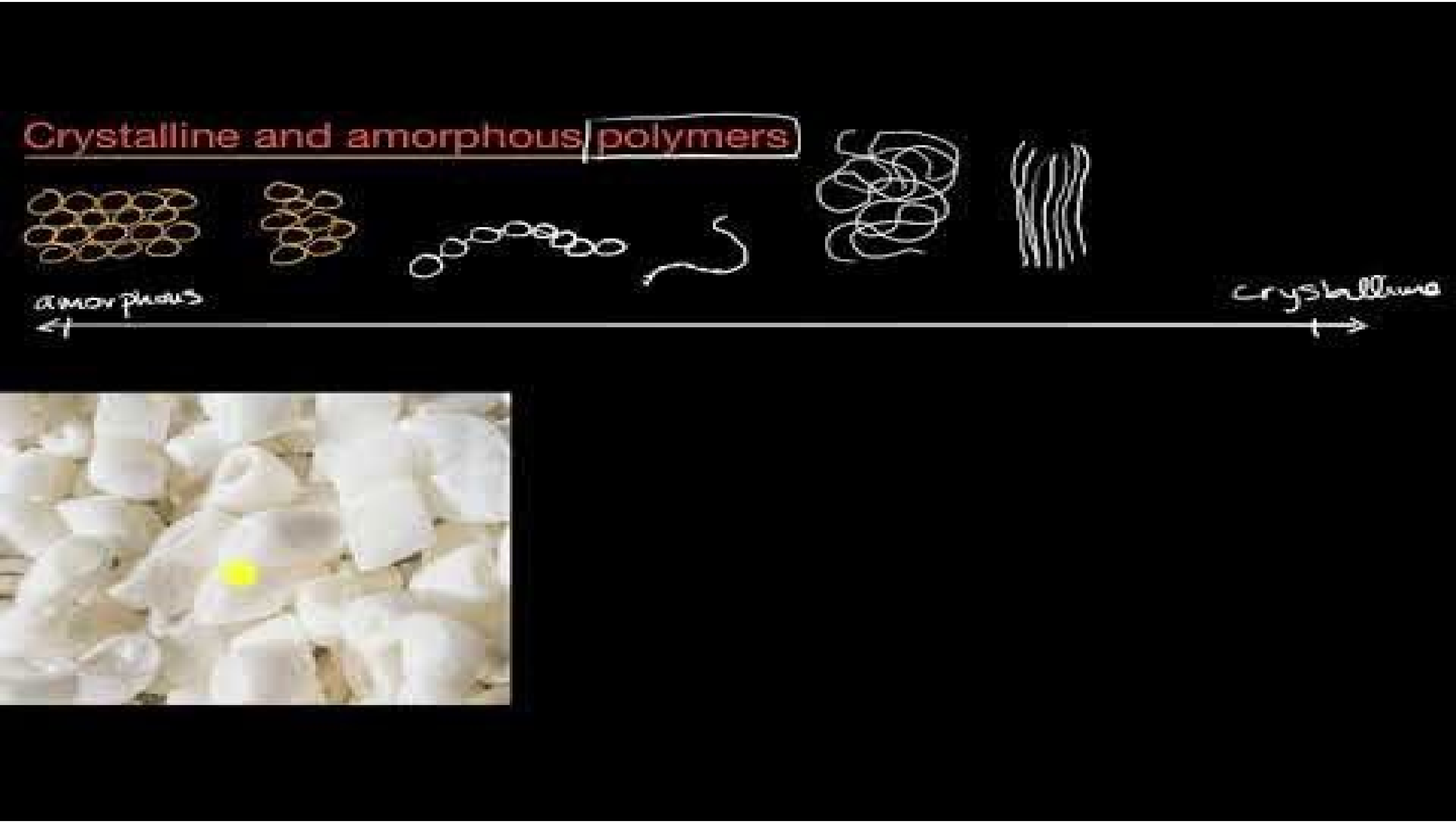


- ***Amorphous*** :
  - Literally "without structure"
  - No repeating array



- ***Semi-crystalline*** :
  - Structure containing regions of both crystalline and amorphous molecular arrangements




Crystalline and amorphous polymers
amorphous
crystalline

# Crystallinity in Polymers

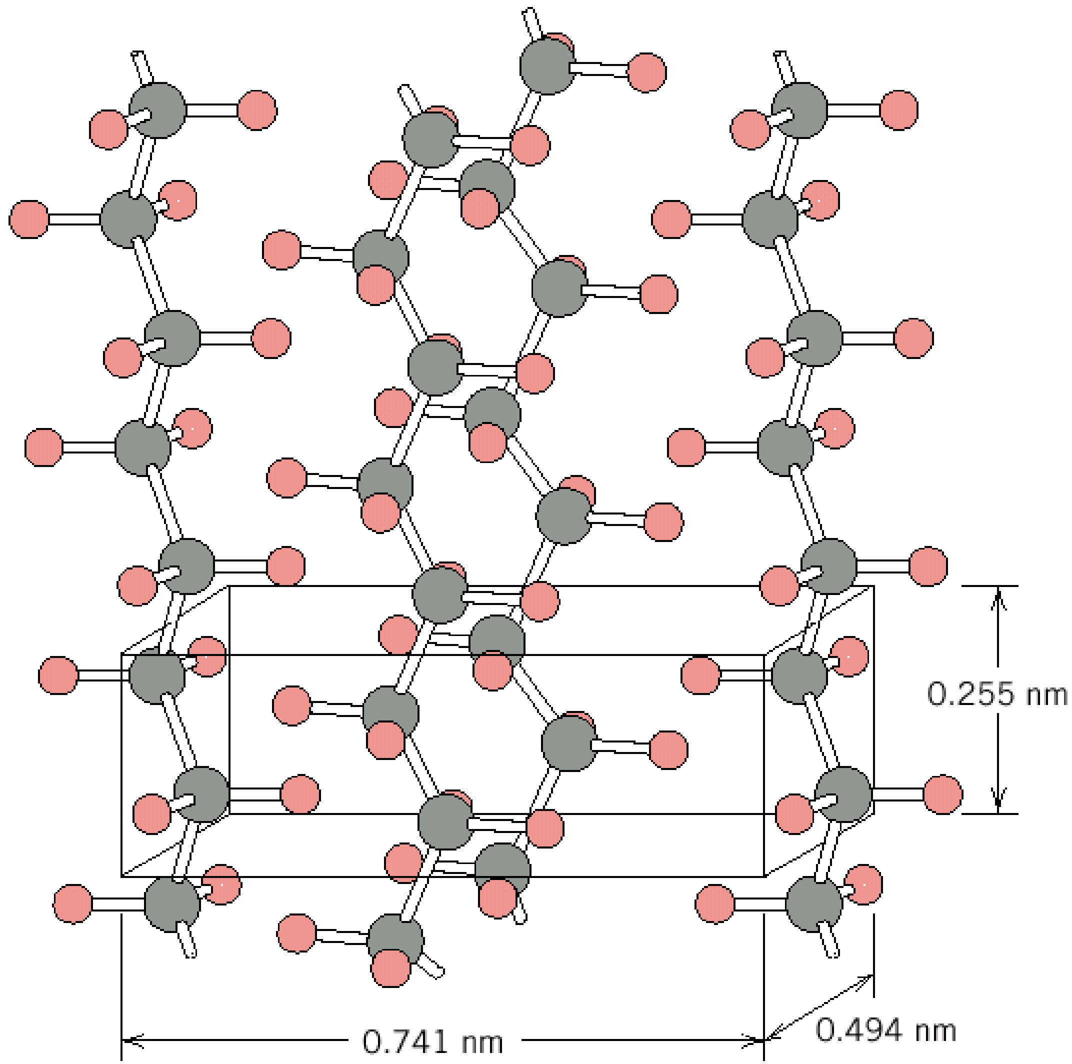
Adapted from Fig. 14.10, *Callister & Rethwisch 8e.*

Ordered atomic arrangements involving molecular chains

Crystal structures in terms of unit cells

Example shown

- polyethylene unit cell

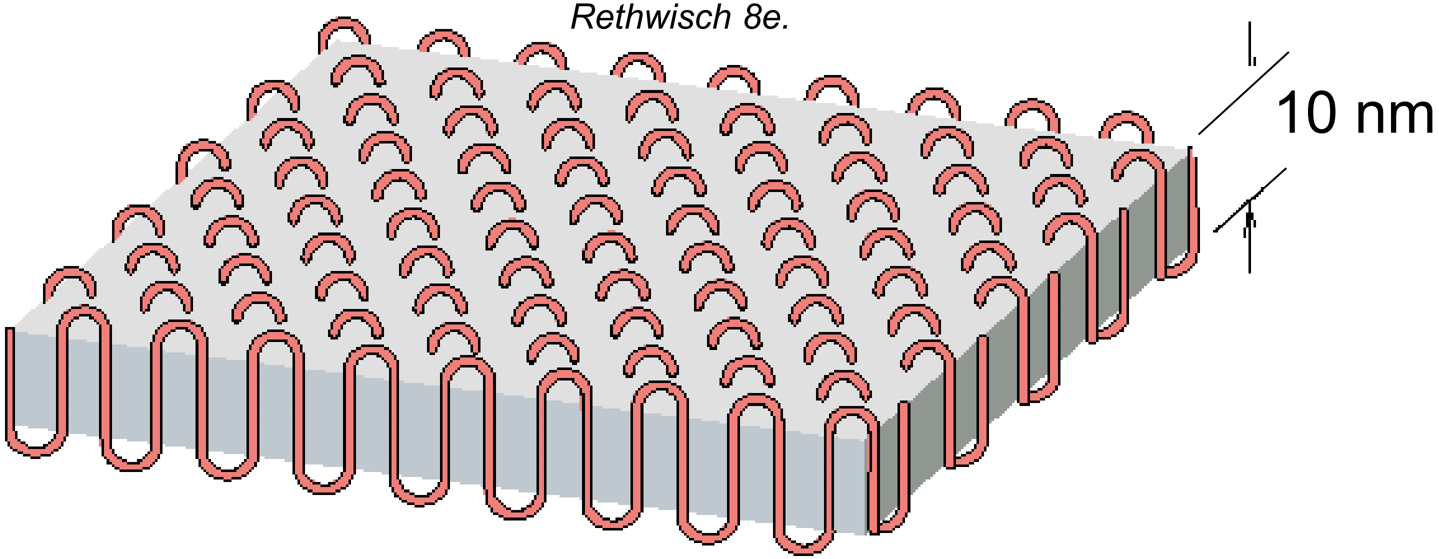


# Polymer Crystallinity

Crystalline regions

- thin platelets with chain folds at faces
- Chain folded structure

Adapted from Fig. 14.12, *Callister & Rethwisch 8e.*




- The crystalline state may exist in polymeric materials. However, since it involves molecules instead of just atoms or ions, as with metals or ceramics the atomic arrangement will be more complex for polymers.

- There are ordered atomic arrangements involving molecular chains

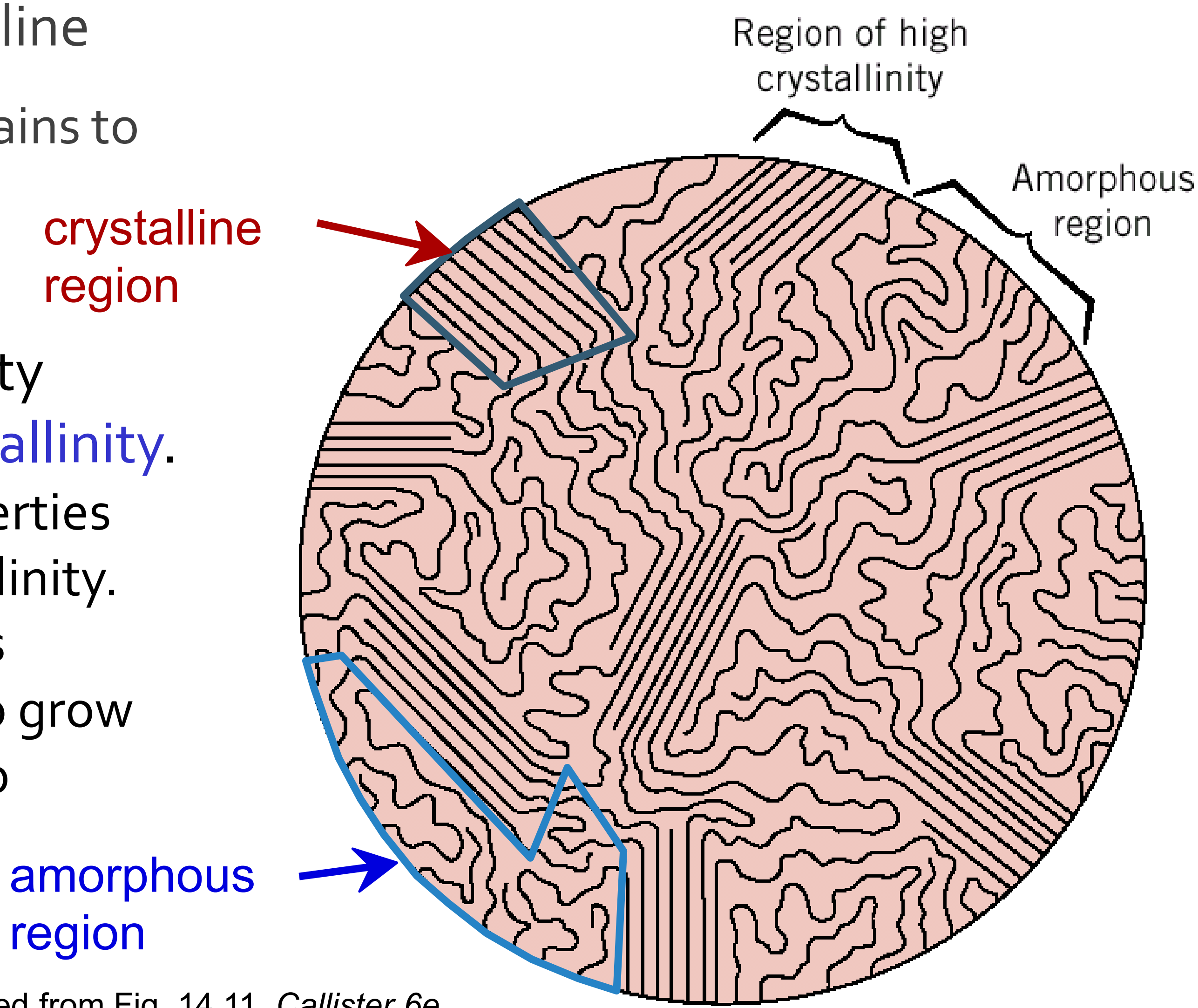
# Polymer Crystallinity (cont.)

Polymers rarely 100% crystalline

Difficult for all regions of all chains to become aligned

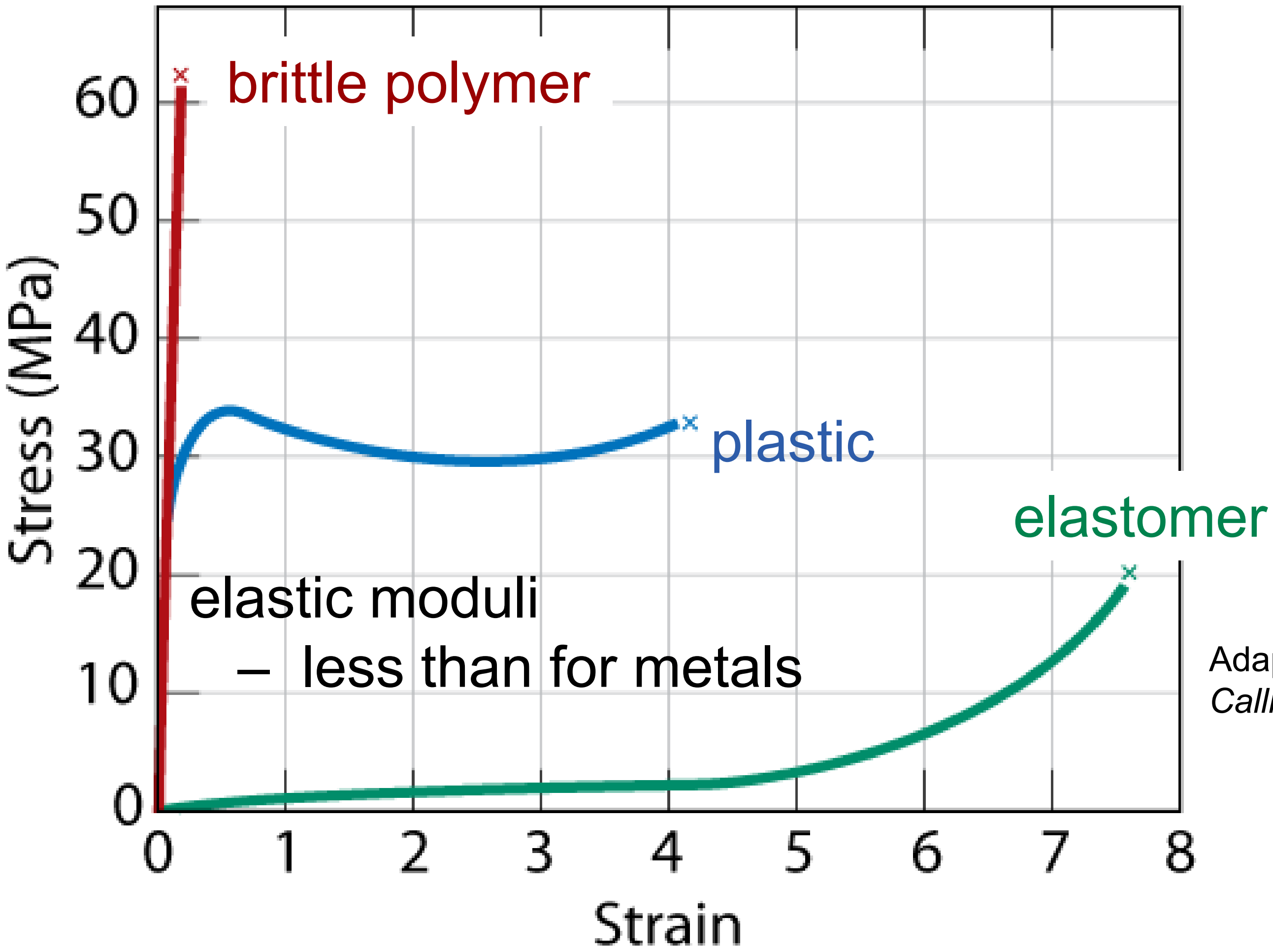
- Degree of crystallinity expressed as % crystallinity.
  -- Some physical properties depend on % crystallinity.
  -- Heat treating causes crystalline regions to grow and % crystallinity to increase.

-- TS and E often increase with % crystallinity.




Adapted from Fig. 14.11, *Callister 6e.* (Fig. 14.11 is from H.W. Hayden, W.G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior*, John Wiley and Sons, Inc., 1965.)

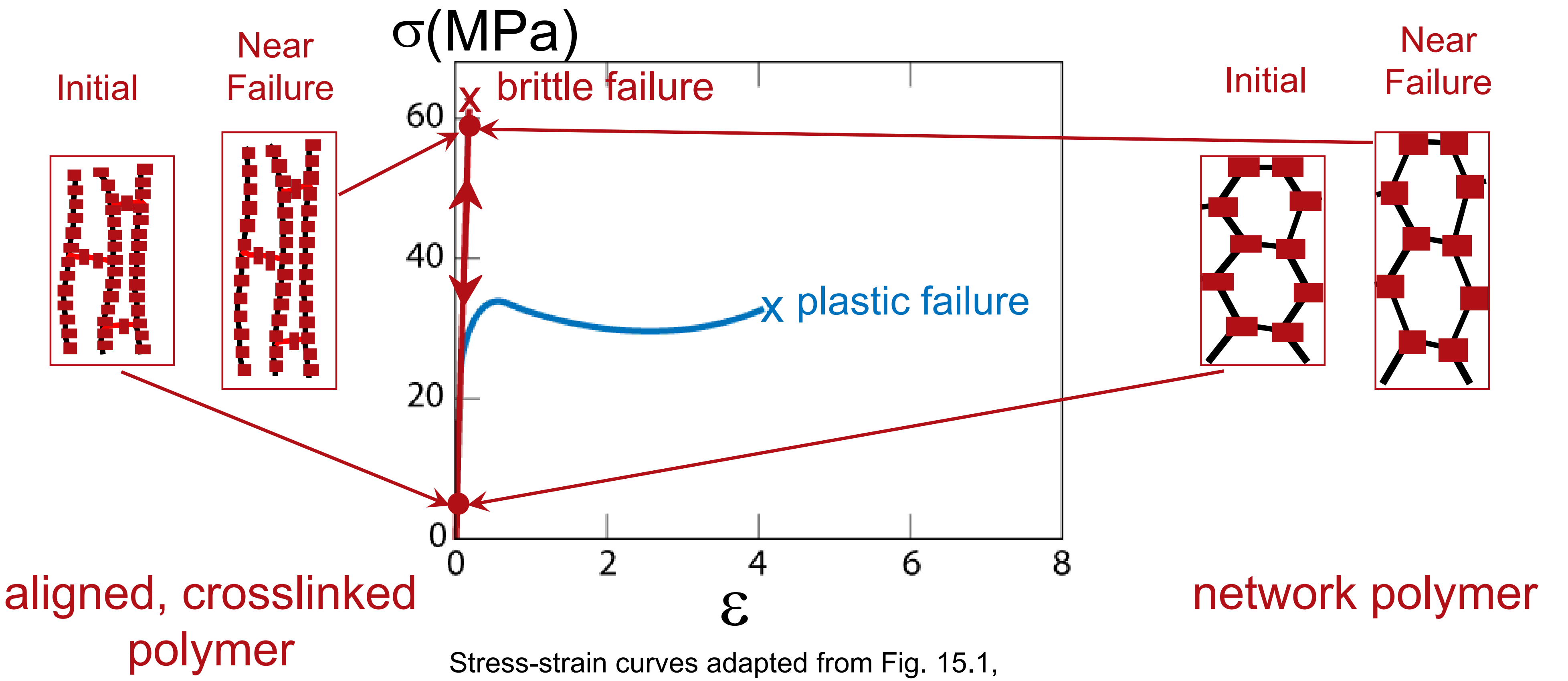
# Mechanical Properties of Polymers – Stress-Strain Behavior




Adapted from Fig. 15.1, *Callister & Rethwisch 8e*.

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

# Mechanisms of Deformation—Brittle Crosslinked and Network Polymers

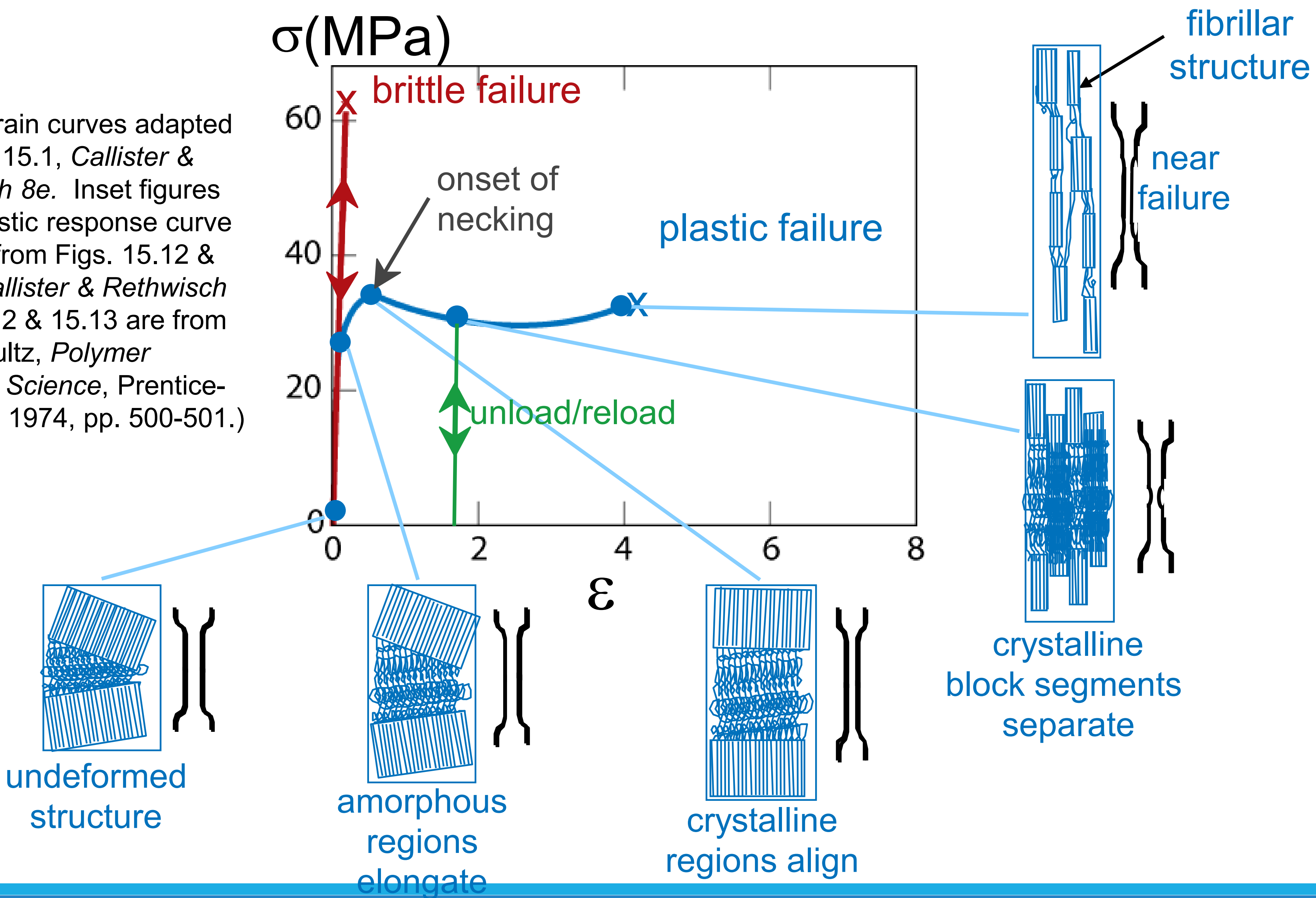



Stress-strain curves adapted from Fig. 15.1, *Callister & Rethwisch 8e.*


35

# Mechanisms of Deformation — Semicrystalline (Plastic) Polymers

Stress-strain curves adapted from Fig. 15.1, *Callister & Rethwisch 8e.* Inset figures along plastic response curve adapted from Figs. 15.12 & 15.13, *Callister & Rethwisch 8e*. (15.12 & 15.13 are from J.M. Schultz, *Polymer Materials Science*, Prentice-Hall, Inc., 1974, pp. 500-501.)

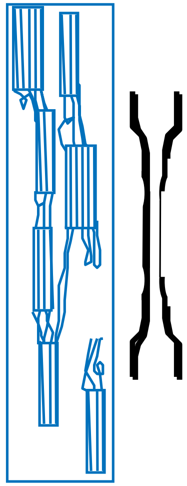




36

# Predeformation by Drawing

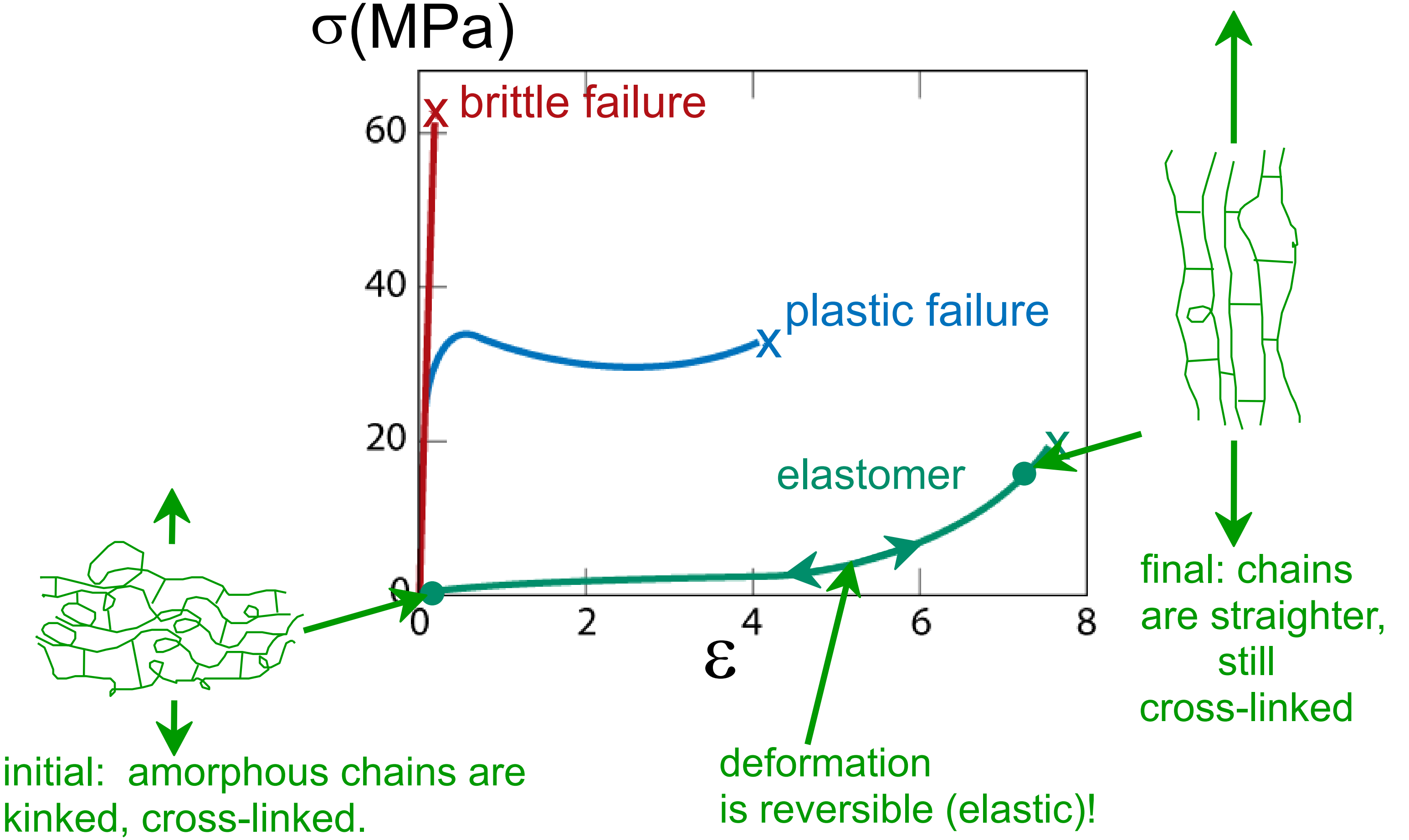
- Drawing...(ex: monofilament fishline)
  -- stretches the polymer prior to use
  -- aligns chains in the stretching direction
- Results of drawing:
  -- increases the elastic modulus (*E*) in the stretching direction
  -- increases the tensile strength (*TS*) in the stretching direction
  -- decreases ductility (%*EL*)
- Annealing after drawing...
  -- decreases chain alignment
  -- reverses effects of drawing (reduces *E* and *TS*, enhances %EL)
- Contrast to effects of cold working in metals!



Adapted from Fig. 15.13, *Callister & Rethwisch 8e*. (Fig. 15.13 is from J.M. Schultz, *Polymer Materials Science*, Prentice-Hall, Inc., 1974, pp. 500-501.)


37

# Mechanisms of Deformation—Elastomers




Stress-strain curves adapted from Fig. 15.1, *Callister & Rethwisch 8e.* Inset figures along elastomer curve (green) adapted from Fig. 15.15, *Callister & Rethwisch 8e*. (Fig. 15.15 is from Z.D. Jastrzebski, *The Nature and Properties of Engineering Materials*, 3rd ed., John Wiley and Sons, 1987.)

- Compare elastic behavior of elastomers with the:

  -- brittle behavior (of aligned, crosslinked & network polymers), and

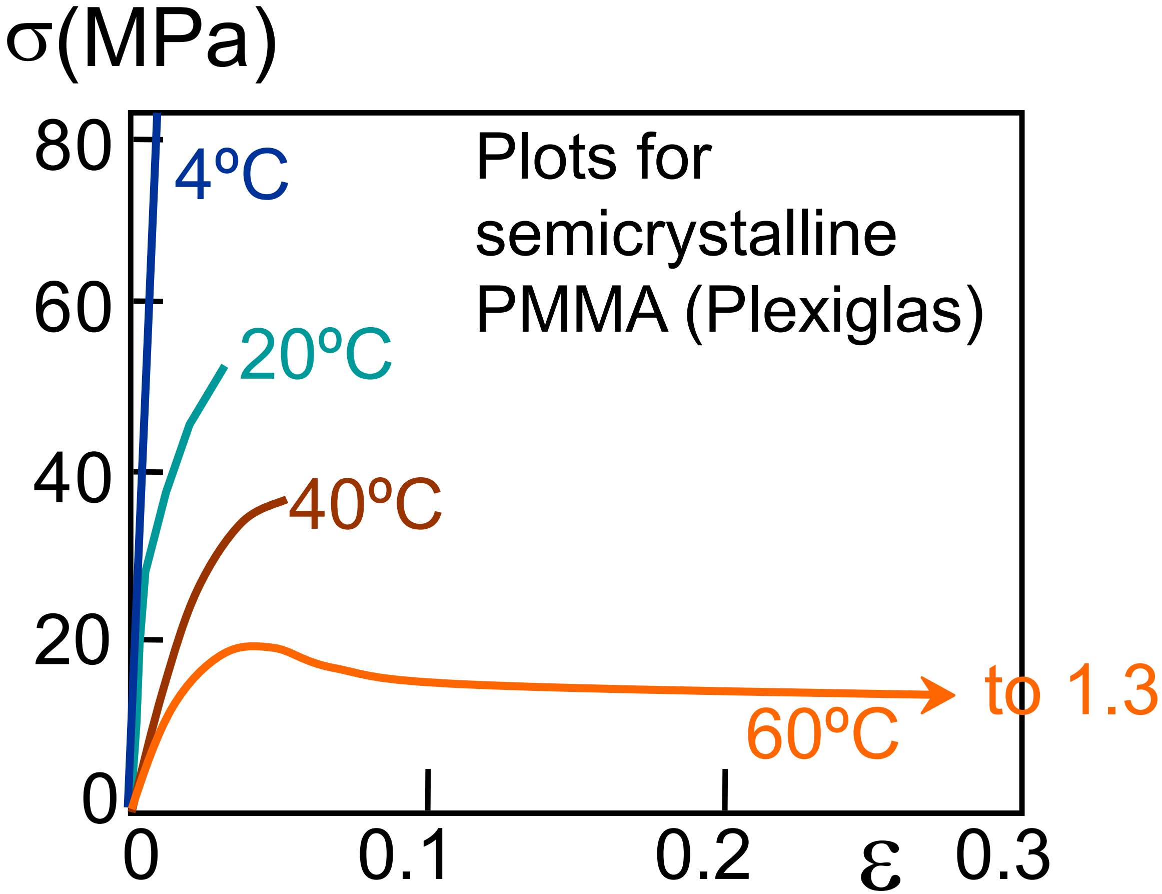
  -- plastic behavior (of semicrystalline polymers)

  (as shown on previous slides)


38

# Influence of Temperature on Thermoplastics

- Decreasing *Temp*...
  - -- increases *E*
  - -- increases *TS*
  - -- decreases *%EL*




Adapted from Fig. 15.3, *Callister & Rethwisch 8e*. (Fig. 15.3 is from T.S. Carswell and J.K. Nason, 'Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics", *Symposium on Plastics*, American Society for Testing and Materials, Philadelphia, PA, 1944.)


39

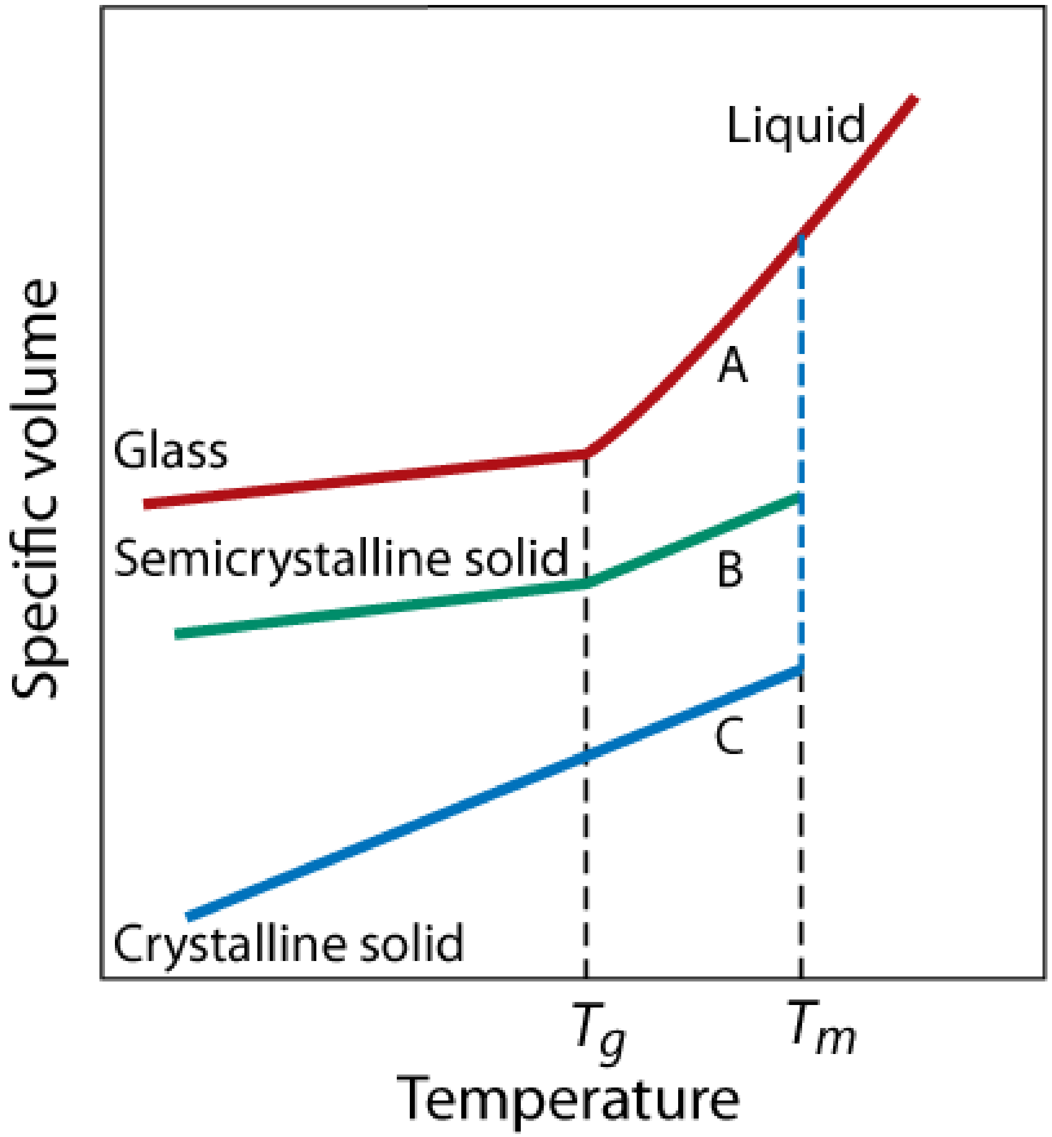
# Melting & Glass Transition Temps.

**Melting Temperature: $T_m$**

- Range of temperature
- Important as it defines temp limits
- For crystalline material there is a discontinuous change in specific volume at $T_m$
- Below this temperature the polymers are soft and flexible and above this the polymer is molten.

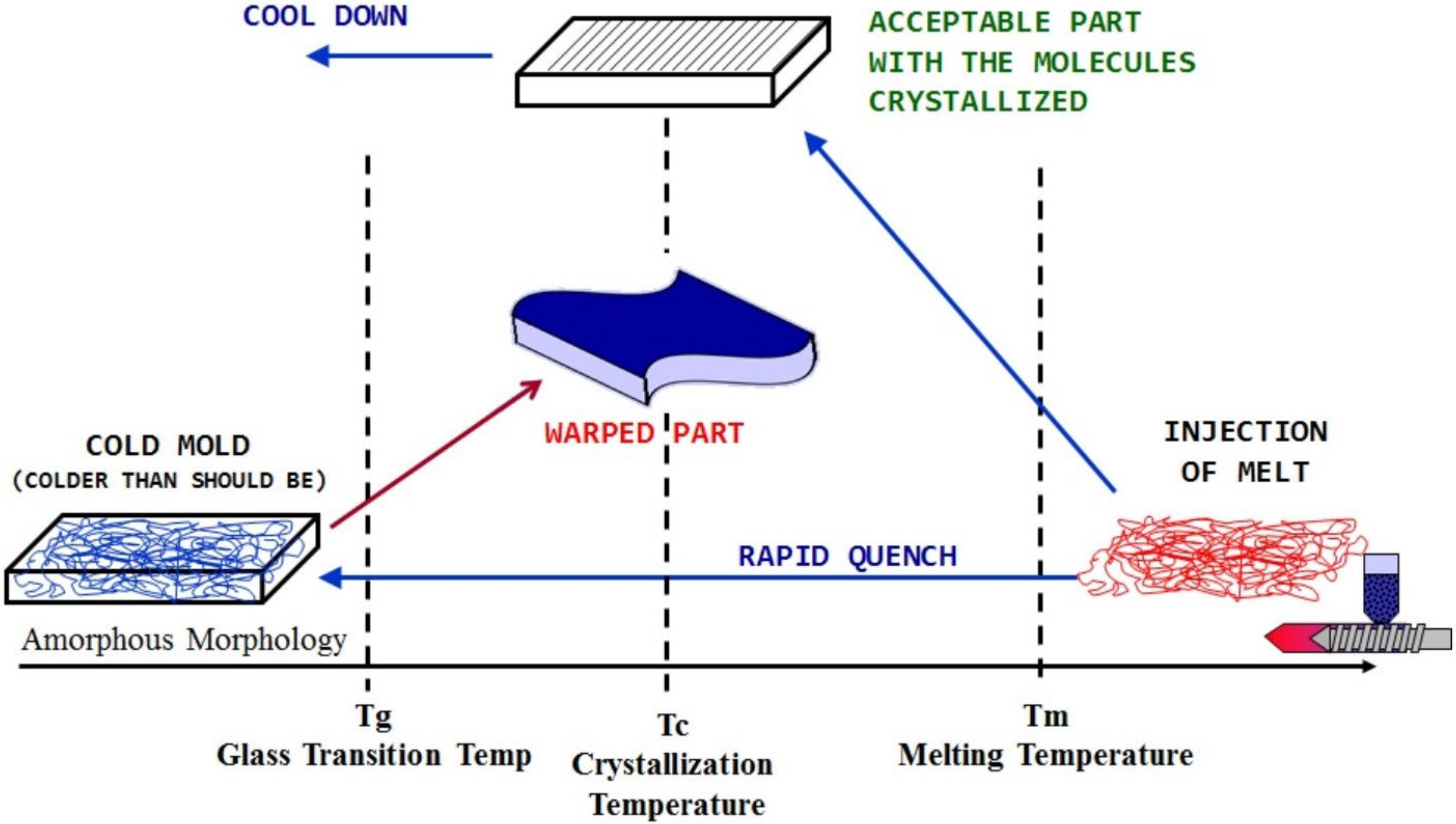
**Glass transition Temperature: $T_g$**

- Amorphous & semicrystalline
- Below this temperature polymers are hard and brittle and above this the polymers are soft and flexible.
- Gradual transformation from liquid to rubbery material to finally a solid state




Adapted from Fig. 15.18, *Callister & Rethwisch 8e.*


40




https://fimmtech.com/knowledgebase-2/polymers-and-plastics/

# Processing of Plastics

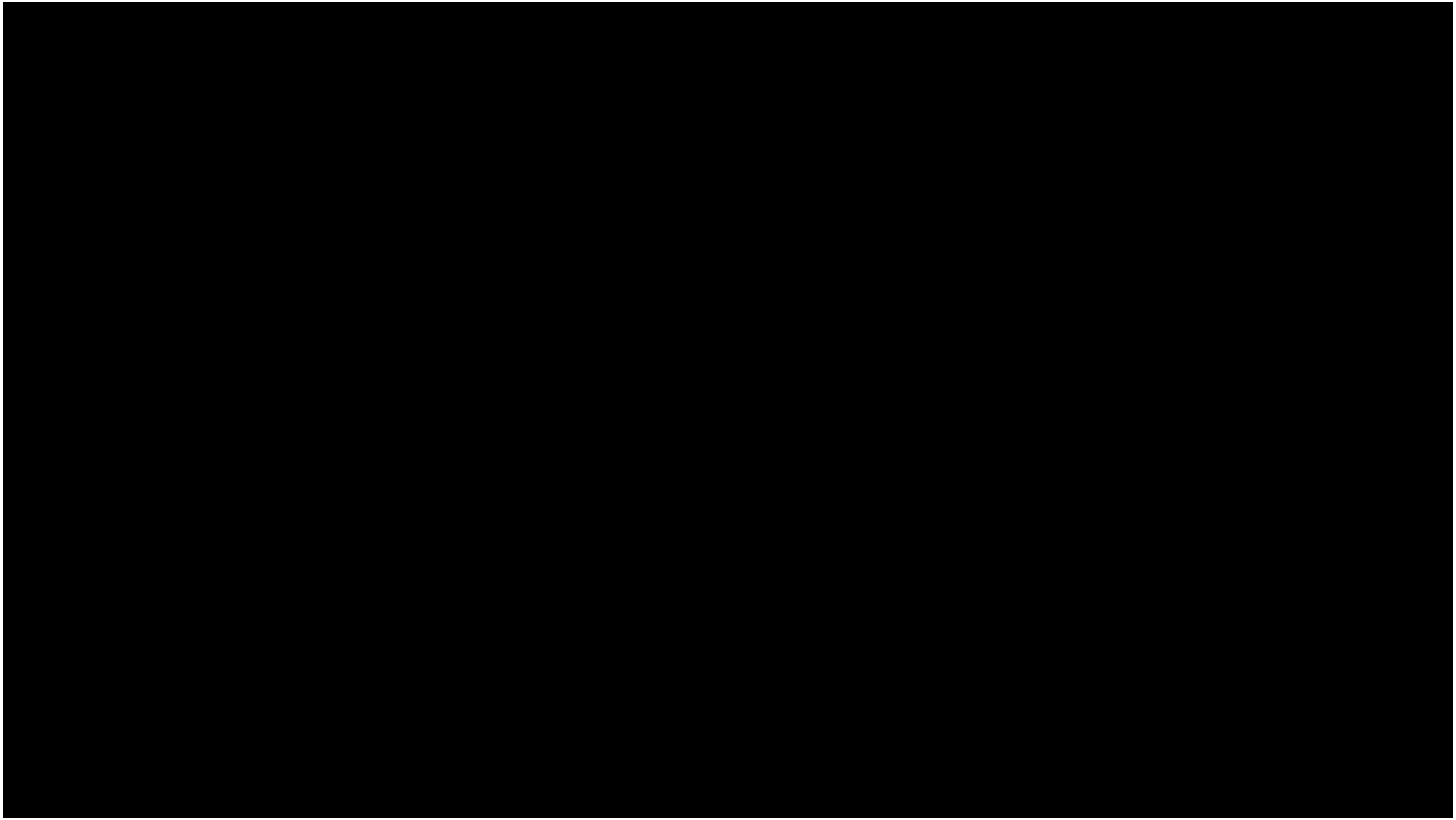
Thermoplastic

- can be reversibly cooled & reheated, i.e. recycled
- heat until soft, shape as desired, then cool
- ex:  polyethylene, polypropylene, polystyrene.

- Thermoset
  - when heated <u>forms a molecular network</u> (chemical reaction)
  - degrades (doesn't melt) when heated
  - a prepolymer molded into desired shape, then chemical reaction occurs
  - ex:  urethane, epoxy


42

# SACMI CCM Continuous Compression Molding for Coffee Capsules



https://youtu.be/qp5JA1YKsOI

# 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

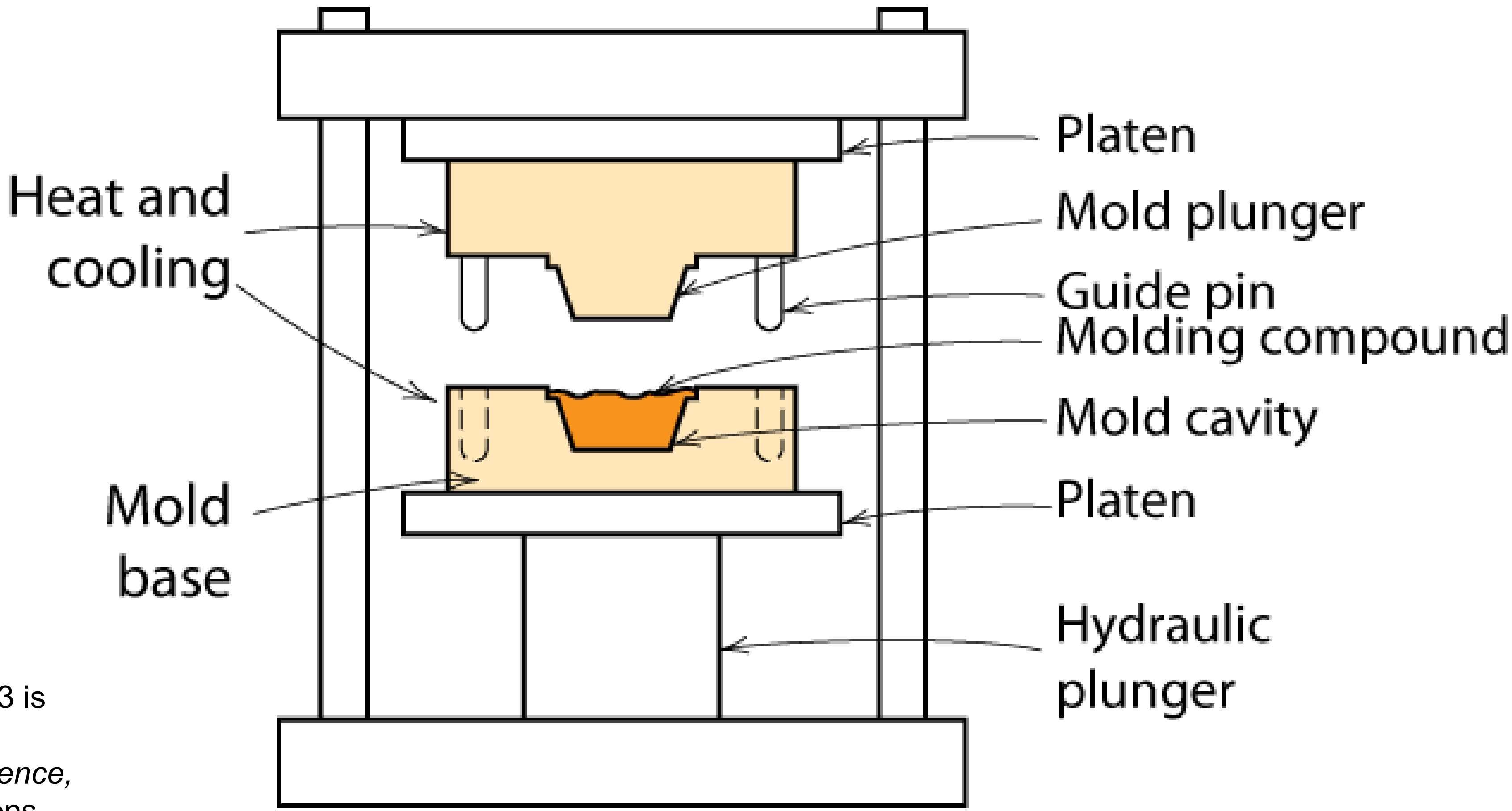
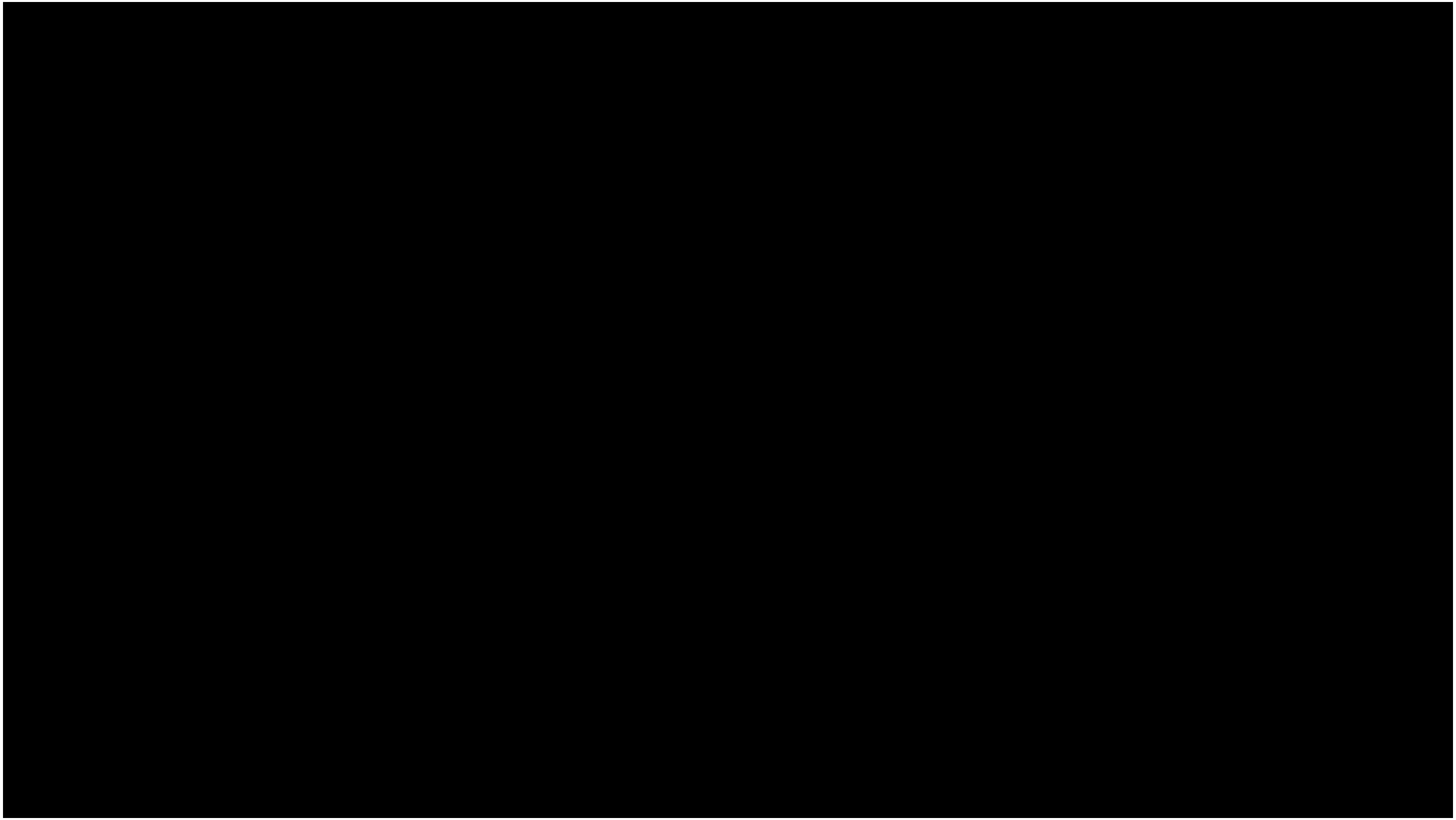



Fig. 15.23, *Callister & Rethwisch 8e*. (Fig. 15.23 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., John Wiley & Sons, 1984.)


44

# Plastic Injection Molding



https://youtu.be/RMjtmsr3CqA

# 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

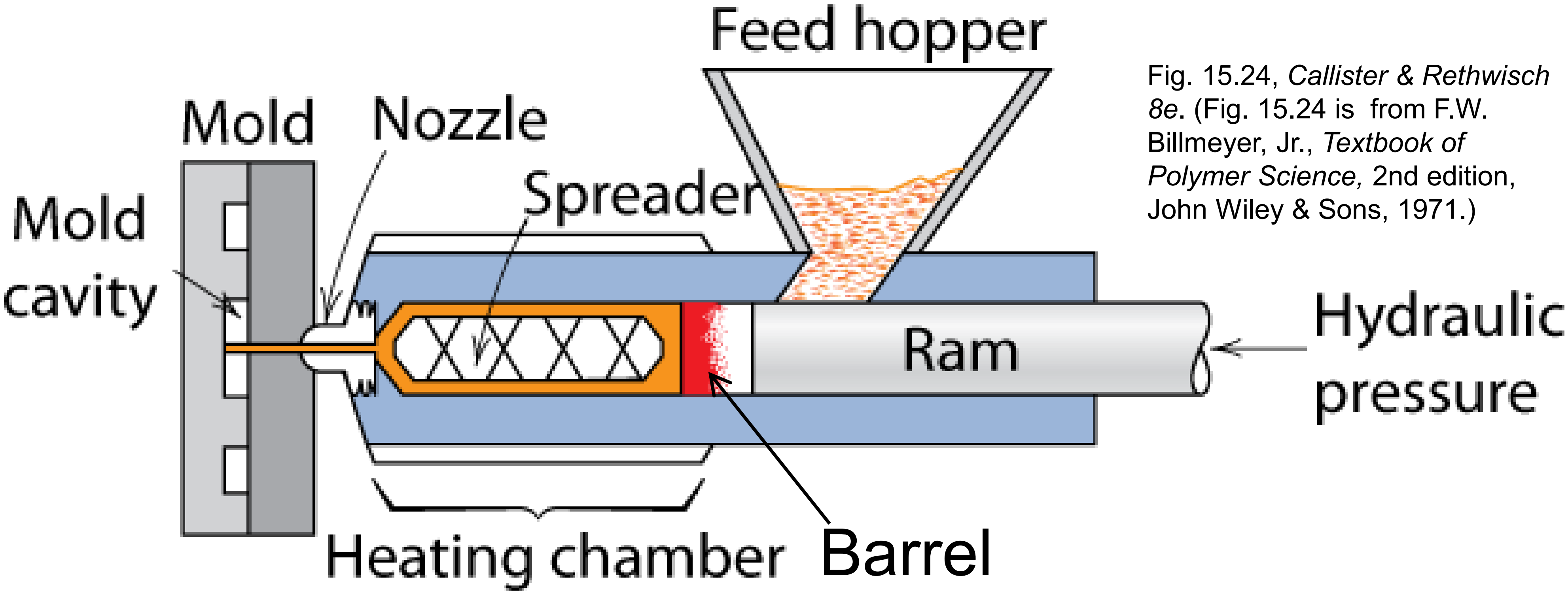
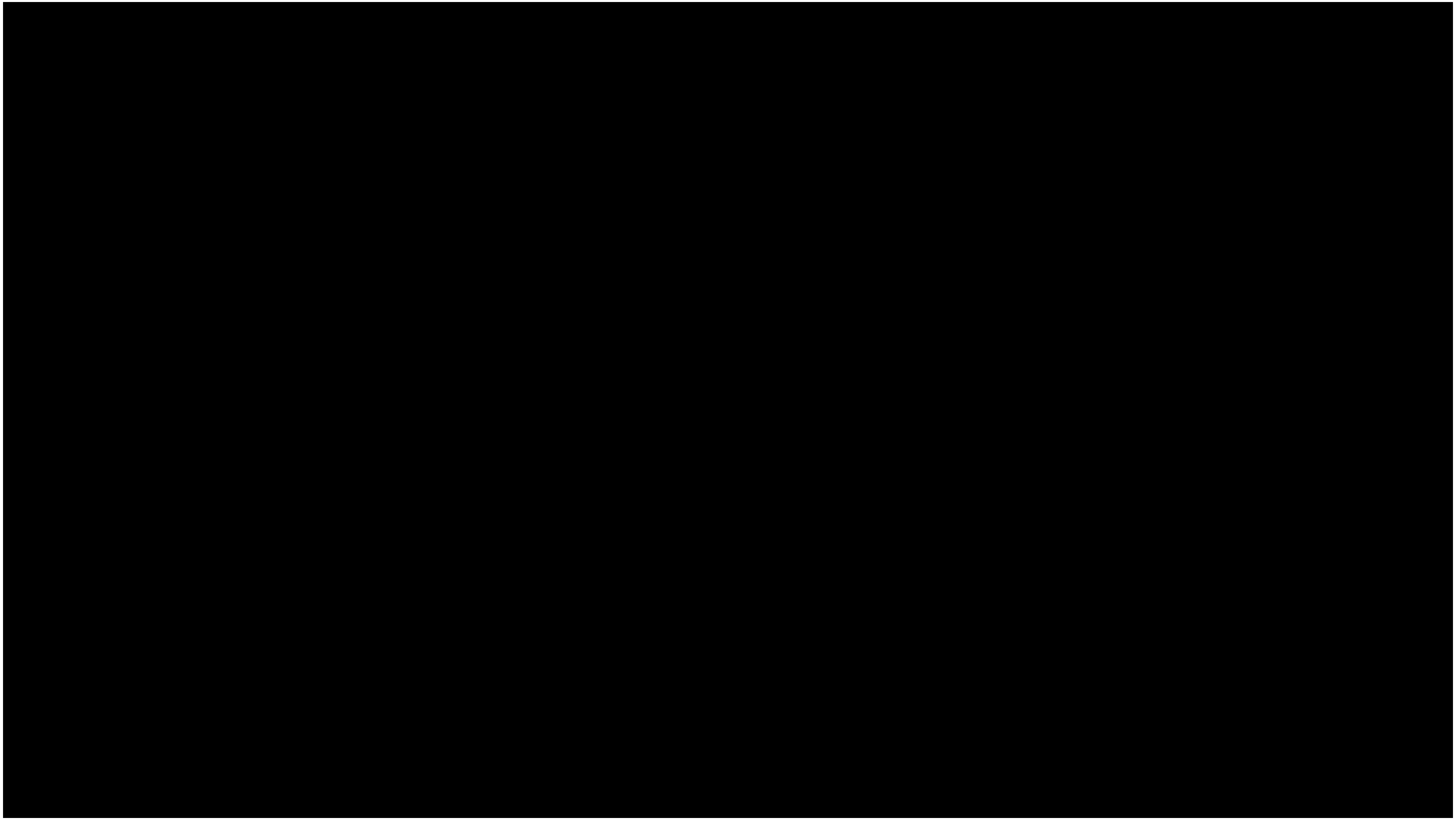



Fig. 15.24, *Callister & Rethwisch 8e*. (Fig. 15.24 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science,* 2nd edition, John Wiley & Sons, 1971.)


46

## Plastic Processing Overview



https://youtu.be/qn16JtE_vLc

# 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 (extrudate)

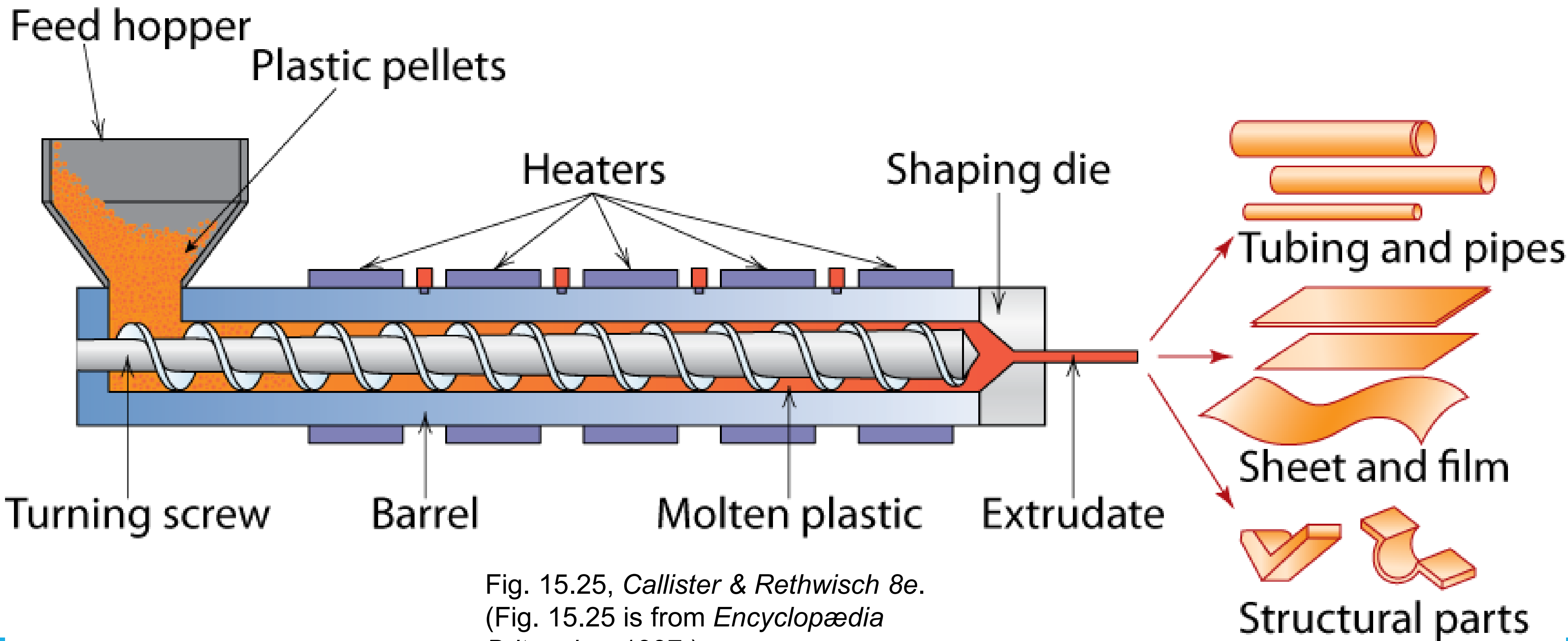



Fig. 15.25, *Callister & Rethwisch 8e*.
(Fig. 15.25 is from *Encyclopædia Britannica*, 1997.)


48

# Processing Plastics – Blown-Film Extrusion

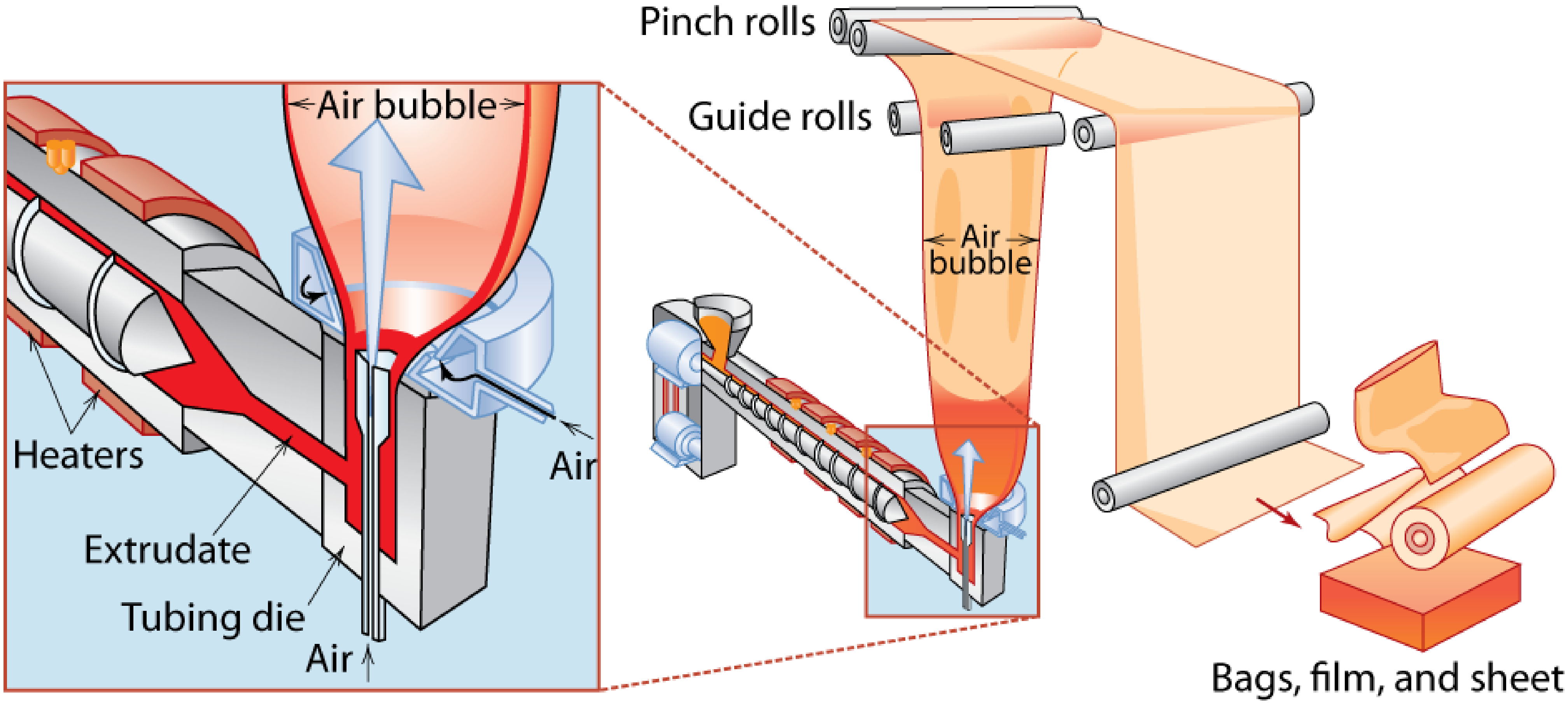



Fig. 15.26, *Callister & Rethwisch 8e*.
(Fig. 15.26 is from *Encyclopædia Britannica,* 1997.)


49

# 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


50

# 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 (adherands)
  - 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


51

# Advanced Polymers

## Ultrahigh Molecular Weight Polyethylene (UHMWPE)

Molecular weight ca. $4 \times 10^6$ 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)


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

# Summary

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

Table 15.3 *Callister & Rethwisch 8e*:

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
-- coatings
-- films
-- advanced polymeric materials
-- fibers
-- adhesives
-- foams